Research Program

Environmental Remediation Technology

Terry C. Hazen

510/486-6223
tchazen@lbl.gov

The Environmental Remediation Technology Program (ERTP) conducts multidisciplinary environmental research on characterization, monitoring, modeling, and remediation technologies. This research is directed primarily at U.S. Department of Energy and Department of Defense waste site problems, as well as pollution problems in California—especially those targeted by the CALFED program for the San Francisco Bay/Delta. Since many of the contaminants or closely related compounds found at these sites are also dominant at industrial waste sites, much of this research is also applicable to problems faced by the private sector and other government agencies. These projects are both basic and applied, and include everything from molecular studies to full-scale field deployments in all types of media (gas, water, sediment), in all types of environments (wetlands to deserts). This year's major customers have been DOE Office of Environmental Management, DOE Office of Science, DOE National Nuclear Security Administration Chemical and Biological Non-Proliferation Program NN-22, Work for Others-DOD, Work for Others-USEPA, Work for Others-CALFED, and Work for Others (Industry and Other Government Agencies).

DEMONSTRATIONS AND DEPLOYMENT

ERTP supports DOE's Office of Environmental Management (EM) in both the areas of Environmental Restoration and the Office of Science and Technology. Berkeley Lab ESD scientists directly supervise characterization, remediation, and monitoring, and provide regulatory and permitting support to Berkeley Lab's Environmental Health and Safety Department for all environmental problems on site. During this past year, the program demonstrated and deployed technologies for thermally enhanced vapor extraction of volatile organic compounds (VOCs), constant-head well testing for characterization of low-yield porous materials, and groundwater flow models for complex geological structures.

This past year, ERTP has developed a new method, implemented in a code called ODA, to analyze the operation pumping rates for underground injection of liquid wastes for the U.S. Environmental Protection Agency. This represents a significant safety enhancement over normal injection practices. ERTP scientists have also shown how strontium isotopes can be used to determine vadose zone infiltration flux and how carbon isotopes can be used to measure biodegradation rates of buried waste by carbon dioxide analyses of soil gas. At DOE waste sites, they have also demonstrated how uranium isotope analysis can be used to determine source histories and migration rates. In addition, ERTP scientists have field-demonstrated a new crosswell high-frequency seismic method for determining nonaqueous-phase liquid (NAPL) contamination in groundwater aquifers. Since NAPL is the hardest contaminant source to detect and remediate, this method could save both time and money in characterization and monitoring during and after remediation.

ERTP also supports EM with technical expertise via the International Programs in Russia, Ukraine, and Argentina; Environmental Laboratory Council, EM Technical Assistance Program, the multi-agency DNAPL Technology Advisory Group, and the Hanford Vadose-Groundwater-River Integrated Program.

FIELD AND LABORATORY STUDIES

DOE's Office of Science provides funding for several ERTP projects. The basic research projects funded in this area take advantage of the unique facilities at Berkeley Lab, such as the Advanced Light Source, where researchers look at the interactions between contaminants, water, and minerals at the microscale. ERTP scientists have also shown how humic acid

accelerates biodegradation of organic contaminants using synchrotron IR methods. Further, ERTP is conducting a project (funded by the Natural and Accelerated Bioremediation Research [NABIR] program) that looks at mesoscale biotransformation dynamics as the basis for predicting core-scale reactive transport of chromium and uranium. The Environmental Management Science Program (EMSP) funds projects on the geochemical evolution of highly alkaline and saline tank waste plumes in vadose zone sediments at DOE waste sites. DOE's Initiatives for Proliferation Prevention program also funds ERTP for bioprospecting in the extreme environments of the Kamchatka Peninsula in Russia.

ERTP efforts have recently achieved numerous scientific breakthroughs and advancement in knowledge. ERTP scientists showed this year that biological treatment of mixed wastes represents a safer alternative to incineration. Using a drip-feed bioreactor, ERTP scientists were able to degrade mixed wastes containing acetonitrile and tritium, so that only the radioactive component remained without dilution. ERTP scientists also developed a new module for the TOUGH2 simulator that models landfill biodegradation processes—to allow landfill management of optimal biodegradation rates for faster and safer closure. Moreover, using EMSP funding, ERTP scientists have developed a new high-frequency electromagnetic impedance measurement system for characterization, monitoring, and verification for buried waste and landfills. ERTP scientists have also demonstrated new techniques for measuring microbial backgrounds in air, using DNA microarrays that can determine variations in community structure from site to site. The effects that perturbations might have on key organisms can thus be determined, as can the reliability of various detection systems.

DEMONSTRATIONS AND TECHNICAL ASSISTANCE FOR INDUSTRY/ OTHER AGENCIES

ERTP has researched selenium transport in the Grassland Water District, California, for many years. Recent research has focused on better methods for compliance monitoring and management. The U.S. Bureau of Reclamation has sponsored this work in an effort to better manage selenium loading in the agricultural wastewater of the San Luis Drain. ERTP scientists showed that real-time management of dissolved oxygen in the San Joaquin River Deep Water Ship Channel was possible. The Sonoma County Water Agency has also funded ERTP scientists to model hydraulic conductivities along the Russian River in northern California, using groundwater temperature profiles. ERTP scientists have also developed a real-time sensor that can monitor suspended sediment loads and streams, and thus improve watershed management.

ERTP also provides technical consultation to private industry and other government agencies on implementing Berkeley Lab- and DOE-patented technologies at private and government-owned sites. Private industry must have a license to the technology for use at private sites, and all ERTP expenses are reimbursed by the company or another agency. Several contracts this year were executed for consultation regarding bioremediation and characterization.

NABIR PROGRAM OFFICE

ERTP continued to be the Natural and Accelerated Bioremediation Research (NABIR) Program Office for the Office of Science. The NABIR Program Office maintains the dynamic NABIR Web home page (www.lbl.gov/NABIR/) with links to investigators, program element managers, science team leaders, recent publications, annual meeting registration, calls for proposals, review documents, and other Web sites. In addition, the NABIR Program Office also organizes the NABIR annual investigators meeting, with more than 150 participants and sessions for posters, presentations, and breakout sessions. Moreover, the NABIR Program Office is producing a new NABIR bioremediation primer that will be available to the public in print or electronically on the NABIR home page. The NABIR program office also assisted DOE-HQ in reviewing and evaluating field-project implementation at the Field Research Center for the NABIR program at Oak Ridge National Laboratory.

PARTNERS AND FUNDING

ERTP receives support from DOE programs in the Offices of Science and Environmental Management. The EM programs include the Environmental Management Science Program (now in the Office of Science); the Subsurface Contaminants Focus Area; and the Characterization, Monitoring, and Sensor Technology Crosscutting Program. The Office of Science funds the NABIR Program Office at Berkeley Lab, and the Office of Science, Office of Biological and Environmental Research funds two environmental remediation projects. The DOE IPP and NN-22 also fund two biological monitoring and bioprospecting projects. Support is also provided by the Department of Defense, Cal-EPA, other DOE Labs, DHS, UC Berkeley, and the U.S. Bureau of Land Management.

DNA Microarrays for Characterization of Microbial Backgrounds

Gary Andersen, Todd DeSantis, and Sonya Murray
Contact: Gary Andersen, 510/495-2795, glandersen@lbl.gov

RESEARCH OBJECTIVES

The primary goal of this project is to understand the quantity and composition of background microorganisms in the environment and to define and predict their ability to interfere with DNA-based pathogen detection systems. By providing baseline knowledge of bacterial organisms in urban aerosols and other environmental samples, this work will make it possible to predict the sensitivity, accuracy, and reliability of DNA-based detection schemes under "real world" conditions. Characterization of bioaerosols is also important for determining the long-term effects of introducing engineered microorganisms for biopesticides and bioremediation on downwind environments.

APPROACH

Sequence variation within the 16S rRNA gene was used to provide an effective method for the identification of bacteria in environmental samples without the need for their cultivation. Taking advantage of the fact that all bacteria possess a 16S rRNA gene, we developed a high-density oligonucleotide microarray for simultaneous identification of all bacterial components in any complex environmental sample. Multiple, sequence-specific probes target sections of the gene that are unique to each species. The combinatorial power of multiple probes increases the confidence of correct species identification. Our latest design has 500,000 probes arrayed on a 1.3 cm^2 surface. The unique discriminatory power of this microarray allows, for the first time, a high-throughput method for fine-scale microbial species composition measurements. Thus, it is possible to measure, over time, the fate of hundreds of different species in a complex microbial community subject to meteorological or other variations.

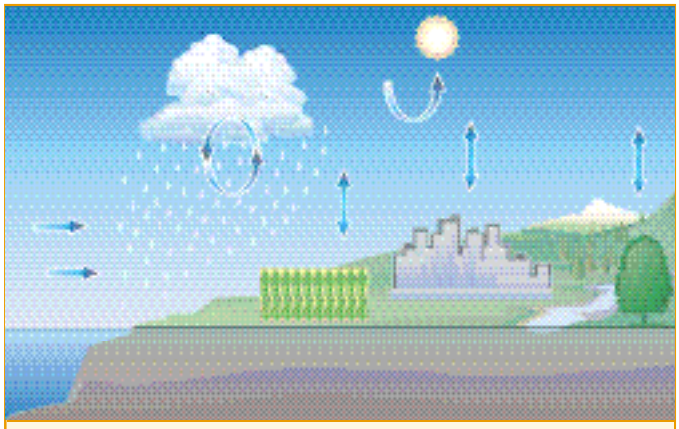


Figure 1. The microbial composition in the atmosphere is highly dynamic. Organisms are released into the air from both local and long-range sources.

ACCOMPLISHMENTS

We collected replicated aerosol samples from two biosurveillance studies targeting 12 U.S. cities and from an eight-site longitudinal transect comparing urban and rural bacterial community composition. Changes in microbial community composition were observed from city to city and from urban to rural areas. Information on bacterial species composition and relative amounts as determined by the strength of the hybridization interaction is being placed on a database. An information retrieval network is being established that will allow researchers to identify predominant organisms for specific cities, seasons, or other user-defined variables.

SIGNIFICANCE OF FINDINGS

Variations from site to site suggest that local reservoirs play a significant role in bacterial community composition. The increased diversity of urban sites over rural sites further strengthens this observation, with a greater number of distinctive habitats in the urban areas. The sequence-specific hybridization of 16S rRNA to a microarray allows the gathering of detailed information on microbial composition and diversity for any environmental sample. By comparing the microbial species composition before and after an environmental perturbation, key organisms may be identified.

RELATED PUBLICATIONS

Wilson, K. H., W.J. Wilson, , J.L. Radosevich, T. Z. DeSantis, V. S. Viswanathan, T.A. Kuczmarski, and G.L. Andersen, High density microarray of small subunit ribosomal DNA probes. Appl. Env. Micro., 68 (5), 2535–2541, 2002.

DeSantis, T. Z., I. Dubosarskiy, and G.L. Andersen, Comprehensive aligned sequence construction for automated design of effective probes (CASCADE-P) using 16S rDNA. Bioinformatics, 19 (July 2003 issue).

ACKNOWLEDGMENTS

This work was supported by the National Nuclear Security Administration (NNSA) Chemical and Biological Non-Proliferation Program, NN-22, for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Smart Storage of Landfilled Waste

Sharon E. Borglin, Terry C. Hazen, Curtis M. Oldenburg, and Peter T. Zawislanski
Contact: Sharon E. Borglin, 510/486-7515, seborglin@lbl.gov

RESEARCH OBJECTIVES

Although Subtitle D landfills are permitted to contain only nonhazardous municipal solid waste (MSW), in fact they often include substances such as metals, solvents, halogenated organics and mercury. Currently, most landfills are "dry tombs" because moisture and air exposure are restricted, slowing biodegradation of the waste and increasing the time required for landfill stabilization. The time period over which the waste presents itself as a risk for contamination of air and water extends to decades, severely limiting land reuse options. In addition, landfill costs have more than doubled in the last 15 years, as the requirements for stabilization and containment of waste have become increasingly stringent, and obtaining a permit for a new landfill site has become more costly.

Smart Storage is the active control of the waste containment environment for accelerated degradation and stabilization of landfill waste. Smart Storage provides a framework for managing landfilled waste that includes long-term, cost-effective, and environmentally sustainable solutions based on bioreactor technology. Extreme heterogeneity and the large scale of landfills make comparison between the technologies difficult. This study directly compares identical MSW samples in controlled laboratory conditions to give relative rates of settlement, gas production, and leachate quality to support the decision-making process concerning aerobic and anaerobic strategies.

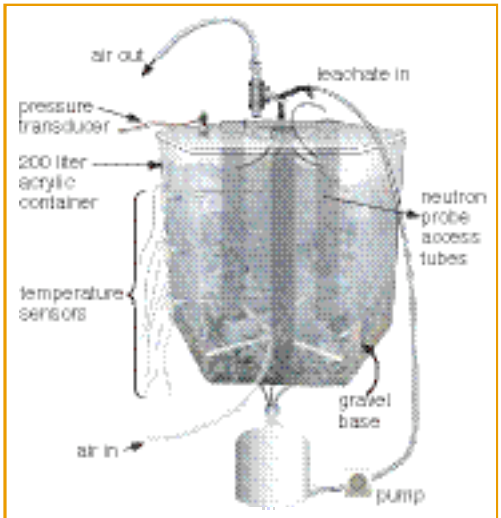


Figure 1. Schematic of the laboratory landfill bioreactor

APPROACH

Mesoscale laboratory reactor systems (see Figure 1) filled with MSW were used to measure respiration rates, methane and carbon dioxide generation rates, subsidence, and leachate quality. Three treatments were applied to the bioreactors: (1) aerobic landfill (air injection with water addition and leachate recirculation), (2) anaerobic landfill (no air injection, water addition and leachate recirculation) and (3) no treatment (no air injection or leachate recirculation), which was converted to a wet, aerobic landfill (air injection with water addition and leachate recirculation).

ACCOMPLISHMENTS

Measurements of leachate quality and gas production clearly demonstrate that aerobic treatment of MSW creates a more stable and environmentally benign waste mass over a shorter treatment time than does anaerobic waste treatment. Comparison of carbon production from both aerobic and anaerobic reactors shows that in the 400-day test period, the aerobic tank produced 6 mol C/kg MSW, whereas the anaerobic bioreactor produced 4 mol C/kg waste. Thus, the aerobic tank was 50% more stabilized than the anaerobic bioreactor. Additionally, methane production was slowed in the anaerobic tank by excess ammonia production, potentially requiring an additional treatment step for removal. Elevated levels of several metals and biochemical oxygen demand were measured in the anaerobic leachate. These leachate quality issues associated with the anaerobic system would require additional investigation.

SIGNIFICANCE OF FINDINGS

This study directly compared identical MSW samples in controlled laboratory conditions to give relative rates of settlement, gas production, and leachate quality to support the decision-making process concerning aerobic and anaerobic strategies. The study shows that although both aerobic and anaerobic treatment is superior to dry-tomb landfill management, the aerobic treatment is a more sustainable and environmentally friendly solution.

RELATED PUBLICATION

Borglin, S.E., T.C. Hazen, C.M. Oldenburg, and P.T. Zawislanski, Comparison of aerobic and anaerobic biotreatment of municipal solid waste. Journal of the Air and Waste Management Association, June 2003 (submited).

ACKNOWLEDGMENTS

This work has been supported by Laboratory Directed Research and Development (LDRD) funding from Berkeley Lab, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Real-time Sensor to Monitor Suspended Sediment Loads in Streams

Chris G. Campbell
Contact: 510/495-2953, cgcampbell@lbl.gov

RESEARCH OBJECTIVES

Throughout California and worldwide, water quality is negatively impacted by suspended sediments in surface water bodies. Not only is sediment itself a major pollutant, but additional contaminants in these environments, including heavy metals and organic compounds like polychlorinated biphenyls, dioxins, and pesticides, are likely to be adsorbed to suspended sediments. Unfortunately, current methods to measure the total mass of suspended sediment mobilized in storm water runoff are inadequate. As a result, it is impossible to accurately estimate the total load of either sediment or associated contaminants transported with sediments during storms.

In response to this challenge, our project developed a fiber-optic in-stream technology (FIT) for continuous measurements of suspended sediment load in surface waterways. Our research objectives were to:

(1) Assemble and test the FIT for light absorbance measurements in suspended sediment solutions.
(2) Address calibration issues.
(3) Compare measurements to a commercially available turbidity probe.
(4) Examine portable and stationary field measurement designs.

APPROACH

The FIT is based on optical light absorbance occurring between two linear fiber-optic arrays. Suspended sediment moving between the source and detector decreases the total light intensity reaching the detector. Light in the red spectra (around 680 nm) was selected to focus on sediment particles. Commercially available turbidity probes measure light scattering at a 90° angle, which is extremely sensitive to sediment geometry (e.g., particle size and shape). The increased sampling size, linear arrangement, and uniquely paired source and detectors make the FIT a superior device for estimating sediment loads.

ACCOMPLISHMENTS

Our proof-of-concept studies examined using a low-energy light source, a red light-emitting diode (LED), connected to a linear fiber-optic array, to measure suspended sediments in a specially designed storm water simulator. Tests examined sediment loads ranging from 1 to 10 g/L, with five particle size classes from 45 to 1,000 mm. We also compared the FIT to a commercially available turbidity probe. Applications of the FIT were successful, with a high signal-to-noise ratio. By adjusting the source-detector spacing, we showed that the linear measurement range may be optimized for a 1 to 10 g/L load (Figure 1). This linear relationship allows for simple device-calibration procedures.

The turbidity probe also measured a linear response to the suspended sediment, but reached a maximum measurement at 3.0 g/L (Figure 1). This maximum may be insufficient in streams that commonly reach maximum loads of 10 g/L during large storms. The variability in turbidity measurements is also much larger than the FIT, because of turbidity's sensitivity to sediment geometry.

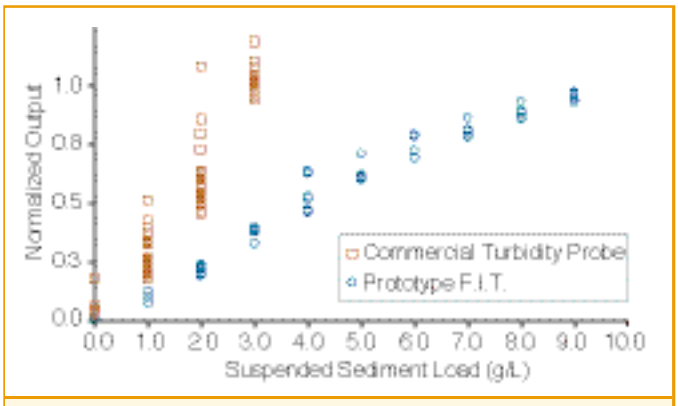


Figure 1. Measurements collected from the prototype FIT (circles) and a commercially available turbidity probe (squares) for suspended sediment loads of 1.0 to 10.0 g/L and for 5 different particle size classes. Data were collected in the laboratory using a specially designed storm water simulator. The Y-axis is the measurement value normalized between 0 and 1.

SIGNIFICANCE OF FINDINGS

The FIT is an accurate, simple to calibrate, inexpensive, and reliable alternative to turbidity measurements for real-time measurements of suspended sediment loads in streams. The application of devices like the FIT could provide information that would ultimately improve stream water quality.

ACKNOWLEDGMENTS

The author would like to thank Danny Laycak, Jim Richards, and Bill Hoppes of Lawrence Livermore National Laboratory. A portion of this work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48, funded by the Laboratory Directed Research and Development Program (LDRD), provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

A Stochastic Integrated Approach to Parameter Estimation Using Geophysical Data

Jinsong Chen, Susan Hubbard, Michael G. Hoversten, and Ernest Majer
Contact: Jinsong Chen, 510/486-6842, jchen@lbl.gov

RESEARCH OBJECTIVES

Subsurface investigations often require characterizing hydrogeological and geochemical parameters. Well-log or core methods for collecting these data are invasive and laborious, and are therefore rarely acquired at a sufficient spacing for describing field conditions. Integrated approaches, which combine multiple sources of information such as wellbore and geophysical measurements, offer great potential for improved, minimally invasive, and cost-effective characterization. Deterministic integration methods, however, are limited because of their inability to solve for a large number of unknown parameters, or to find a global optimal solution, or to describe the uncertainty associated with those parameters. We have developed a stochastic integrated approach that overcomes these limitations, based on the Markov chain Monte Carlo (MCMC) method. This approach has been applied to two different data sets in order to demonstrate the benefits of the method for integrating multiple sources of information.

APPROACH

Our integration framework is based on a Bayesian estimation approach. Within this framework, all unknown quantities are considered as random variables, and observable parameters are considered as data with measurement errors. The unknown variables and the known data are linked by geophysical forward models, rock physical relationships, and the site-specific cross correlations between all the parameters. Those variables, data, and relationships together define a joint conditional probability function (or posterior probability function). Our goal was to obtain the marginal posterior probability function for each unknown variable by conditioning on all the available information. Since analytical methods are not tractable when the joint probability function includes such a large number of unknown variables and when the relationships are very complicated, we use the MCMC method to obtain many samples for each unknown random variable. Using the generated samples, the mean, variance, prediction intervals, and posterior probability function of the unknown variable can be calculated.

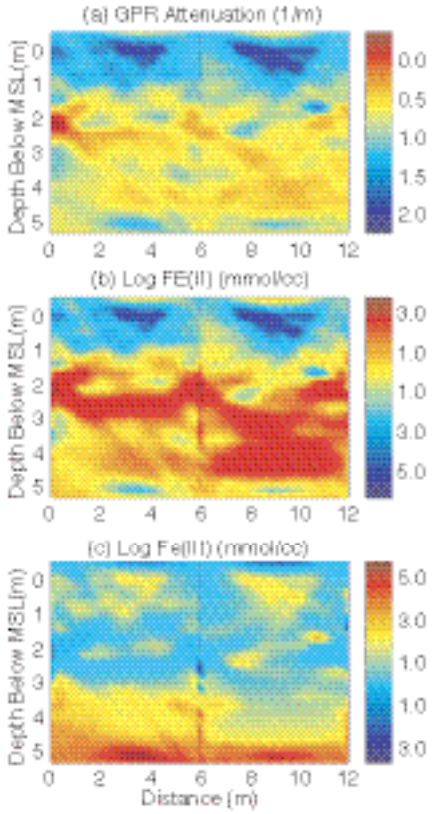


Figure 1. An example illustrating the use of our stochastic integration approach for geochemical parameter estimation. In this study, ground penetrating radar attenuation tomographic data (a) and other types of wellbore data were used to estimate logarithmic extractable Fe(II) (b) and Fe(III) (c) concentrations along a two-dimensional cross section.

ACCOMPLISHMENTS

We employed the developed stochastic model with crosshole ground-penetrating radar attenuation data to estimate sediment geochemical parameters at the South Oyster Bacterial Transport Site in Virginia (Figure 1). We also employed the method with crosshole seismic and electromagnetic data to estimate reservoir parameters, such as porosity and water saturation. Results from the two case studies showed that the developed method was more accurate, flexible, and efficient than deterministic approaches for integrating multiple sources of parameter-estimation information.

SIGNIFICANCE OF FINDINGS

We have developed a general framework that can be used to integrate various types of data sets for parameter estimation. This is the first effort to use minimally invasive and cost-effective geophysical data to aid in estimation of field-scale geochemical parameters. The methodology is particularly advantageous for use with data sets involving a large number of variables and complicated relationships between the variables.

RELATED PUBLICATIONS

Chen, J., S. Hubbard, Y. Rubin, C. Murray, E. Roden, and E. Majer, Geochemical characterization using geophysical data: A case study at the South Oyster Bacterial Transport Site in Virginia. Water Resources Research, 2003 (in press).

Chen, J., and M.G. Hoversten, Joint stochastic inversion of geophysical data for reservoir parameter estimation. 73rd Annual International Meeting, Society of Exploration Geophysics, 2003 (submitted).

ACKNOWLEDGMENTS

This study was supported by the Assistant Secretary for Energy Research, Office of Biological and Environmental Research, of the U.S. Department of Energy under Contract No. DE-AC03-765SF00098, by NSF Grant EAR 9628306, and by the Assistant Secretary for Fossil Energy, National Petroleum Office, of the U.S. Department of Energy, also under Contract No. DE-AC03-76SF00098.

Identifying the Sources of Subsurface Uranium Contamination at the Hanford Site, Washington

John N. Christensen, P. Evan Dresel[1], Mark Conrad, Kate Maher, and Donald J. DePaolo
[1]Pacific Northwest National Laboratory (PNNL)
Contact: John N. Christensen, 510/486-6735, jnchristensen@lbl.gov

RESEARCH OBJECTIVES

In the mid-1990s, a groundwater plume of uranium (U) and other contaminants was recognized in monitoring wells in the B-BX-BY Waste Management Area (WMA) at the Hanford Site in Washington. This area had been used since the late 1940s to store high-level radioactive waste and other products of U fuel-rod processing. Consequently, within a small area there are a number of potential sources for contamination. Some records exist of inadvertent waste spills, and several locations of vadose zone contamination had been identified. Two of these plumes were cored in an effort to understand the extent and nature of the contamination. However, the pattern of U concentration in these cores did not fully resolve the source issue. We undertook a study of the variation in U isotopic composition within the vadose zone and groundwater U plumes to better understand the source and history of contamination, as well as its transport in the subsurface.

APPROACH

The isotopic composition of natural U contrasts with the variable isotopic composition of U from processed fuel rods. This variation can be used as a tracer and fingerprint of contamination. We applied a new technique using MC-ICP-MS to provide high-precision isotopic measurements of small U samples, generating $^{234}U/^{238}U$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$ ratios. Samples were provided from two cores (E33-45 and E33-46; see inset to Figure 1) through vadose zone plumes of U contamination near two single-shelled tanks in the B-BX-BY WMA. Uranium from pore waters in the sediment samples were separated and analyzed for isotopic composition. Aliquots of groundwater samples taken from wells in the area (see inset to Figure 1) were also analyzed. These samples cover the known extent of the groundwater U contamination plume. The results of the isotopic analyses are evaluated and compared to each other to identify sources and the extent of mixing with background U.

ACCOMPLISHMENTS

Twenty-five samples from the two cores were analyzed, along with nine groundwater samples. The results of the analyses are displayed in Figure 1. The isotopic signature of the E33-45 core contamination plume matches the most contaminated groundwater samples. In addition, the isotopic variation of the groundwater samples can be explained by mixing between natural background U and the E33-45 contamination U. The vadose zone plume in the E33-46 core was probably not a significant source of groundwater contamination.

SIGNIFICANCE OF FINDINGS

A comparison of the U isotopic data to model histories of fuel rod isotopic compositions demonstrates that the E33-45 contamination is consistent with a large spill event in 1951, as had been suspected from historical records. The locus of this spill is about 150 m from the core of the groundwater plume, suggesting significant horizontal displacement of the contamination before it encountered the water table. Over 50 years separates the vadose zone spill and the groundwater contamination detected in the mid-1990s, indicating a continuing large potential for contamination. Between 1993 and 2001, it appears that the groundwater U contamination migrated at an average of ~0.7 m/day. High-precision U isotopic measurements provide an improved tool for tracing and understanding the behavior of U contamination in the subsurface and groundwater.

ACKNOWLEDGMENTS

This work was supported by the Assistant Secretary of the Office of Environmental Management, Office of Science and Technology, Environmental Management Science Program, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 to Berkeley Lab and Contract No. DE-AC06-76RL01830 to Pacific Northwest National Laboratory.

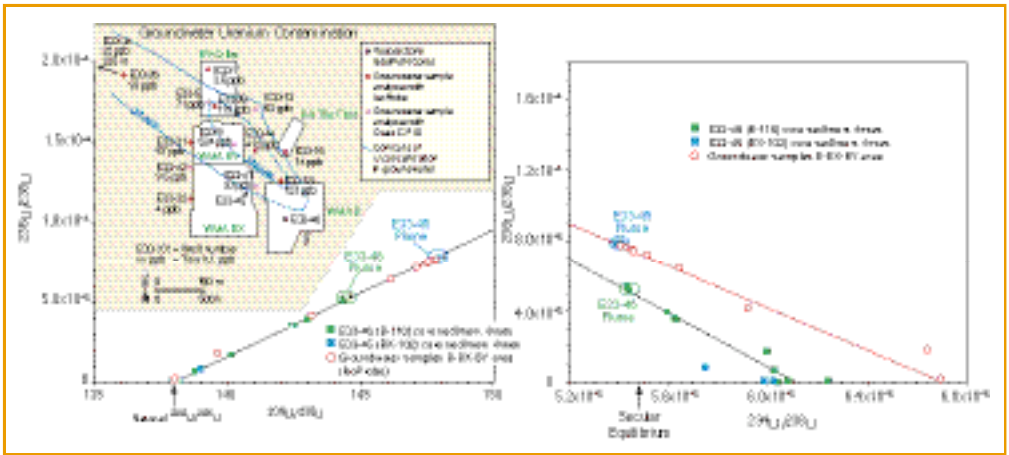


Figure 1. Uranium isotopic data for groundwater (red circles) samples, and sediment pore water from cores E33-45 (blue squares) and E33-46 (green squares). Left panel $^{238}U/^{235}U$ vs. $^{236}U/^{238}U$ and right panel $^{234}U/^{238}U$ vs. $^{236}U/^{238}U$. Inset in left panel is a map of analyzed sample well and core locations in the B-BX-BY Waste Management Area.

Estimation of Natural Biodegradation Rates of Organics in Buried Waste at INEEL

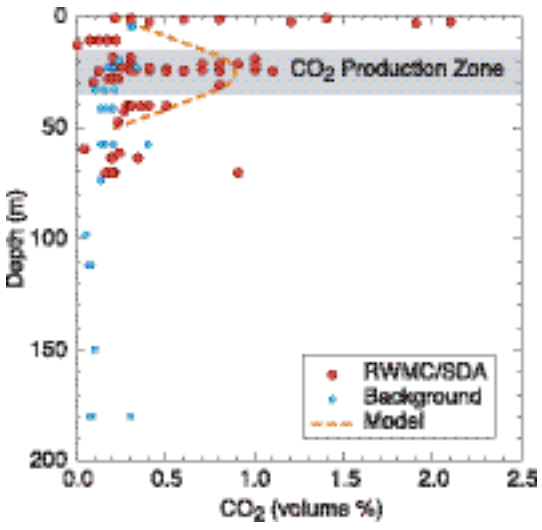
Mark Conrad and Donald J. DePaolo
Contact: Mark Conrad, 510/486-6141, msconrad@lbl.gov

RESEARCH OBJECTIVES

Radioactive waste resulting from U.S. Department of Energy activities is buried in shallow pits in the Subsurface Disposal Area (SDA) at the Radioactive Waste Management Complex (RWMC) of the Idaho National Engineering and Environmental Laboratory (INEEL). In addition to the radionuclides, the waste drums also contain significant amounts of chlorinated solvents mixed with lubricating oils. Leakage from the drums has resulted in a plume of vapor-phase contaminants in the vadose zone. The main objective of this study was to use measurement concentrations and isotopic compositions of CO_2 from the SDA to assess the potential for bioremediation of the organic contaminants at the site.

APPROACH

Over a 2-year period, pore gas samples were collected from monitoring wells in and around the RWMC site. Gas sampling ports within the monitoring wells were designed for sampling discrete depth intervals. Sampling depths ranged from <1 m to 180 m. For each sample, the CO_2 concentration and stable carbon isotope ratios ($\delta^{13}C$ values) were measured. In addition, the ^{14}C contents of a subset of these samples were also measured.



Fgure 1. Concentrations of CO_2 versus sampling depth for samples from monitoring wells in the Subsurface Disposal Area (red circles) and from background wells (blue circles) adjacent to the site. The dashed orange line corresponds to CO_2 concentrations calculated for a 20 m thick production zone (the shaded area between 15 m and 35 m) with CO_2 concentrations averaging 0.9% (versus 0.2% in the background wells).

ACCOMPLISHMENTS

Carbon dioxide concentrations in pore gas samples from monitoring wells in the vicinity of the disposal pits were 3 to 5 times higher than the concentrations in nearby background wells. The $\delta^{13}C$ values of CO_2 from the disposal pits averaged 2.4‰ less than CO_2 from the background wells, indicating that the elevated CO_2 concentrations around the pits were derived from source materials with $\delta^{13}C$ values in the range of -24‰ to -29‰. These $\delta^{13}C$ values are typical of lubricating oils, but higher than most solvents. The radiocarbon (^{14}C) contents of CO_2 across most of the site were significantly elevated above modern concentrations because of reactor blocks buried in a subsurface vault at the site. However, several samples collected from the high-CO_2 zone on the far side of the RWMC from the reactor blocks had very low ^{14}C contents (less than 0.13 times modern), confirming production from lubricating oils manufactured from fossil hydrocarbons.

SIGNIFICANCE OF FINDINGS

The key aspects of the data collected for this project include the following:

- The higher concentrations of CO_2 in the pore gas samples from the vicinity of the disposal pits indicate elevated levels of subsurface microbial activity.
- The lower $\delta^{13}C$ values of the CO_2 in the disposal area suggest that the source of the elevated CO_2 concentrations is organic carbon.
- ^{14}C contents of less than 13% of modern indicate that biodegradation of fossil hydrocarbon compounds in the waste material is the primary source of the CO_2.

A simple 1-dimensional production-diffusion model of the CO_2 anomaly observed at the site is consistent with intrinsic biodegradation rates on the order of 0.5 to 2.0 metric tons of carbon per year. This represents degradation of approximately 1% per year of the lubricating oils buried in the disposal pits.

RELATED PUBLICATION

Conrad, M.E., and D.J. DePaolo, Carbon isotopic evidence for biodegradation of organic contaminants in the shallow vadose zone of the Radioactive Waste Management Complex. The Vadose Zone Journal, 2003 (in press).

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Environmental Management Science Program, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

DOE Environmental Management International Projects Highlights

Boris Faybishenko
Contact: 510/486-4852, bafaybishenko@lbl.gov

BACKGROUND AND OBJECTIVES

Berkeley Lab is involved in eight projects with Russia, Ukraine, and Argentina. The projects with Russia are conducted according to a "Memorandum of Cooperation in the Areas of Environmental Restoration and Waste Management" between DOE and the Ministry of Atomic Energy for the Russian Federation. The projects with Argentina are being conducted according to the "Implementing Arrangement" between DOE and the National Atomic Energy Commission of the Argentine Republic. The collaboration with Ukraine is provided in accordance with the agreement between the U.S. and Ukraine governments concerning the International Radioecology Laboratory of the International Chernobyl Center.

The overall goal of these projects is to assess and improve the capability of the DOE's fate and transport models in predicting future environmental and human impacts of radioactive contaminant releases. The international sites chosen will benefit from application of the latest U.S. models, while DOE will benefit from access to long-term and detailed monitoring data sets of contaminant transport in a variety of contaminant, climatic, and geological settings.

APPROACH AND ACCOMPLISHMENTS

The projects with Russia include predictions of transport of radionuclides (^{90}Sr, ^{137}Cs, ^{238}U, and ^{239}Pu) and nitrates in the groundwater at the Mayak and the Lake Karachay sites (which are among the most radioactively contaminated sites in the world). Models for deep well injection of liquid radiation waste have been developed for the Tomsk site. In addition, conceptual and numerical models have been developed for vadose zone flow and transport at two field sites (Novo-Voronezh and Tomsk), as well as comparison of modeling and experimental data for calibrating the numerical models.

The International Radioecology Laboratory in Ukraine provides services to researchers from Texas Tech University and the Savannah River Ecology Laboratory to conduct their research in the Chernobyl Exclusion Zone. A Special Issue of the International Journal of Environmental Sciences and Pollution Research (ESPR) devoted to problems arising from the Chernobyl Nuclear Power Plant accident of 1986 is being edited and prepared for publication, including manuscripts submitted from Ukraine, Canada, U.S., and Russia.

The projects with Argentina include: (1) numerical modeling and characterization of groundwater flow and contaminant transport at the Ezeiza nuclear waste disposal site, with recommendations for appropriate monitoring technologies; and (2) investigations of the physics of liquid flow and contaminant transport to develop improved conceptual and mathematical modeling for unsaturated fractured-porous media.

SIGNIFICANCE OF FINDINGS

These projects will allow DOE researchers, engineers, and managers to use international scientific resources to test and build confidence in DOE's fate and contaminant transport models and remediation technologies, and to reduce the costs and increase the predictability of remediation technologies during long-term stewardship of DOE sites.

ACKNOWLEDGMENTS

This work was supported by the Assistant Secretary of the Office of Environmental Management, Office of Science and Technology, Environmental Management Science Program, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The aforementioned projects are managed by the Joint Coordinating Committee for Environmental Restoration and Waste Management (JCCEM) of DOE and the Institute for International Cooperative Environmental Research of Florida State University.

NAPL Contaminant Location with High-Frequency Crosswell Seismic Methods

Jil T. Geller, Ernest L. Majer, Jonathan Ajo-Franklin, Kenneth H. Williams, and John E. Peterson
Contact: Jil T. Geller, 510/486-7313, jtgeller@lbl.gov

RESEARCH OBJECTIVES

Our objectives are to develop, demonstrate, and evaluate, at appropriate field sites, the utility of high-frequency seismic imaging methods to detect and characterize nonaqueous-phase liquid (NAPL) contamination in groundwater aquifers.

APPROACH

This work is a new application of Berkeley Lab's high-frequency crosswell seismic imaging system. Crosshole seismic data is obtained at sites known to have NAPL contamination to map the distribution of P-wave velocities and amplitudes between boreholes (tomograms). Several approaches are tested to distinguish anomalies arising from the presence of NAPL from those arising from lithological heterogeneities, including: (1) time-lapse measurements before and after remediation, (2) comparison of tomograms from the contaminated location with nearby clean locations, (3) calibration of field data with laboratory measurements on cores from the site with varying amounts of NAPL, and (4) constraint of seismic data with crosswell radar data.

ACCOMPLISHMENTS

We obtained baseline crosswell data (before remediation) at two contaminated sites where remediation is currently in progress. We also measured P-wave transmission on cores from one of the sites, as a function of NAPL/water saturation. At the northeast site of the former DOE Pinellas Plant in Florida, NAPL trichloroethylene (TCE), toluene, methylene chloride, weathered oils, and resins all contaminate the 30 ft deep surficial aquifer. In laboratory tests on core from selected survey boreholes, NAPL TCE and toluene caused significant reductions in P-wave velocity and increases in P-wave attenuation relative to water-saturated conditions. Our crosswell seismic and radar surveys, within and outside of the area identified as having NAPL, reveal continuous sedimentary layers where NAPL could be trapped. Regions of anomalously high P-wave attenuation occur throughout the surveyed region, which may arise from lithology, biogenic gas, NAPL, or a combination of these. At the Paducah Gaseous Diffusion Plant in Kentucky, we collected crosswell seismic data at the location of a historic TCE spill, estimated to be as large as 500,000 gallons, before beginning a demonstration of six-phase heating remediation. Crosswell data in a NAPL-free area showed generally consistent lithology, with measurable differences, compared to the contaminated site.

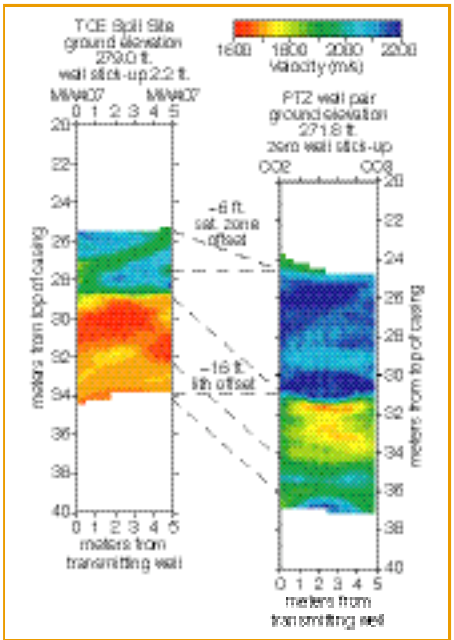


Figure 1. Velocity distributions between survey wells at the Paducah Gaseous Diffusion Plant before the onset of remediation. The tomogram on the left is at the site of the TCE spill. The right hand image is from wells outside the Plant boundary where there is no dense nonaqueous-phase liquid (DNAPL) TCE. The same lithological contrasts occur at each site, and the offsets between the layers are consistent. Changes in these distributions in postremediation surveys will indicate whether the lower velocities at the TCE spill site are caused by DNAPL.

SIGNIFICANCE OF FINDINGS

The contrast in the acoustic velocities of many NAPL contaminants (such as TCE and toluene) in water significantly affect P-wave attributes in natural-aquifer core samples tested in the lab. Possible locations of NAPL areas were identified from comparing P-wave attributes in a nearby uncontaminated zone, but these are uncertain because of the unknown contribution of well-completion and lithology variations. Postremediation surveys will be essential to determine the visibility of NAPL contrasts with water and their signature at the field scale, as well as the efficacy of crosswell seismic imaging for monitoring the remediation of NAPL-contaminated sites.

RELATED PUBLICATIONS

Geller, J.T., J.B. Ajo-Franklin, and E.L. Majer, Effect of immiscible liquid contaminants on P-wave transmission through natural aquifer samples. In Proceedings of the 2003 Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP), Environmental and Engineering Geophysical Society (EEGS), San Antonio, Texas, pp. 1059–1077, April 6–10, 2003; Berkeley Lab Report LBNL-52131.

Ajo-Franklin, J.B., J.T. Geller, E.L. Majer, J.E. Peterson, K.H. Williams, and J.M. Harris, Preliminary characterization of a NAPL-contaminated site using borehole geophysical techniques. In 2003 SAGEEP Proceedings. EEGS, San Antonio, Texas, pp. 202–220, April 6–10, 2003.

ACKNOWLEDGMENTS

This work was funded by the Assistant Secretary of the Office of Environmental Management, Subsurface Contamination Focus Area Program, of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

http://www-esd.lbl.gov/ERT/projects/map_dnapl.html

Biological Treatment of Irrigation Drainage for Selenium Removal

Franklin Bailey Green, Sharon E. Borglin, Clement Hsieh, Rick Y.C. Huang, Tryg J. Lundquist, Nigel W.T. Quinn, Archana Sudame, Mathew G. Takata, and William J. Oswald
Contact: F. Bailey Green, 510/495-2612 ; fbgree@lbl.gov

RESEARCH OBJECTIVES

Much of the subsurface agricultural drainage in the western San Joaquin Valley (SJV) is contaminated with selenate (50–1200 mg/L as Se) and nitrate (20–120 mg/L as N), in addition to high total dissolved solids and boron. This water is currently either discharged to sloughs that drain into the San Joaquin River and then to the San Joaquin Delta, or it is evaporated in terminal ponds. These means of disposal are problematic, since Se is a teratogen that bioaccumulates in the aquatic food web, and nitrate contaminates groundwater supplies and promotes eutrophication of surface waters. Nitrate also interferes with the reduction and removal of selenate SeO_4^{-2}, the most abundant form of Se found in western SJV drainage. Our objective is to develop reliable and economical treatment methods to remove these contaminants.

APPROACH—PILOT FACILITY

We have developed the algal-bacterial selenium removal (ABSR) Process to remove nitrate and selenium from drainage. A 75 m^3/day pilot-scale ABSR Facility has been used to study the mechanisms and rates of selenium and nitrate removal (Figure 1). Subsurface drainage is dosed with a carbon and energy source for bacteria (usually animal feed-grade molasses) and then injected into a baffled and covered anoxic reduction pond. In the reduction pond, bacteria denitrify and reduce selenate to selenite, elemental Se, and bacterial-associated organic Se. Much of the reduced Se settles in the pond. Settled bacterial biomass in the reduction pond undergoes anaerobic decomposition, so that the volume of solid residues increases very slowly. Removal of the selenium-containing solids should not be required for many years, possibly not even decades.

ACCOMPLISHMENTS

Selenium Removal

Over two years, the ABSR Facility at Panoche, California, removed 95% of the influent nitrogen load and 80% of the influent soluble selenium load. The addition of physical-chemical flotation and filtration processes to remove particulate Se has increased total Se removal to 87%. Dozens of bacterial species have been isolated from the ABSR Facility and identified by 16S rRNA sequencing, including the prevalent *Acinetobacter Johnson* II/genospecies 7, *Pseudomonas mendocina*, and *Xanthomonas maltophilia*. Pure cultures of several of these bacteria have been proven to reduce selenite in the laboratory.

Brine Treatment

Planned "zero discharge" drainage management in the SJV will create brines that require treatment. The high salt concentration of brines may inhibit bacterial Se reduction. We have found that denitrification and selenate reduction are unaffected by NaCl concentrations augmented up to 22 g/L. Higher concentrations and other potential inhibitors such as sulfate will be studied during 2003–2004.

SIGNIFICANCE OF FINDINGS

With the ABSR facility at the Panoche Drainage District, we have demonstrated a promising, cost-effective process that will be used in planning full-scale facilities to remove nitrate and selenium from irrigation drainage.

RELATED PUBLICATION

Green, F.B., T.J. Lundquist, N.W.T. Quinn, M.A. Zárate, I.X. Zubieta, and W.J. Oswald, Selenium and nitrate removal from agricultural drainage using the AIWPS® Technology. Fifth International Water Association Specialist Conference on Waste Stabilization Ponds, Pond Technology for the New Millennium, Auckland, New Zealand, April 2–5, 2002; Water Science and Technology, 2003 (in press).

ACKNOWLEDGMENTS

We are grateful to the U.S. Bureau of Reclamation (CALFED Bay-Delta Program), Department of Water Resources, and the Panoche Drainage District for their support.

Figure 1. One of two pilot ABSR Systems at the Panoche Drainage District, San Joaquin Valley, California.

Accelerated Biodegradation of Organic Contaminants by Humic Acid

Hoi-Ying Holman, K. Nieman[1], D.L. Sorenson[1], C.D. Miller[1], and R.C. Sims[1]
[1]Utah State University, Logan, Utah
Contact: Hoi-Ying Holman, 510/486-5943, hyholman@lbl.gov

RESEARCH OBJECTIVES

The role of humic acid (HA) in the biodegradation of toxic polycyclic aromatic hydrocarbons (PAHs) has been the subject of controversy in the design of bioremediation strategy for polluted sites, particularly in unsaturated environments. To solve this controversy, we utilized our novel synchrotron infrared (SIR) spectromicroscopy technique to monitor, *in situ* and over time, the influence of HA on the degradation of pyrene (a model PAH) by a bacterial colony on a magnetite surface.

APPROACH AND ACCOMPLISHMENTS

The pyrene-degrading bacterium used for this study is *Mycobacterium* sp. JLS, a gram-positive, rod-shaped bacterium recently isolated from PAH-contaminated soil at the Libby Groundwater Superfund Site in Libby, Montana. We took time-course "snap shots" of actions of *M.* sp. JLS at the same location on each pyrene-coated sample over more than a month. For comparison, we conducted similar experiments in the absence of either Elliott Soil Humic Acid (ESHA) or bacteria (i.e., abiotic experiments). We summarize in Figure 1 the time-course of pyrene degradation under different experimental conditions over more than a month. We found that, with only slow removal mechanisms, pyrene remains on the mineral surface. For samples occupied by *M.* sp. JLS, ESHA dramatically shortens the onset time for pyrene biodegradation from 168 to 2 hours. Further analysis of spectral fingerprints showed that in the absence of ESHA, it takes the bacteria about 168 hours to produce sufficient glycolipids to solubilize pyrene and make it available for biodegradation. It is likely that the increased bioavailability of pyrene by HA accelerates bacteria-induced degradation.

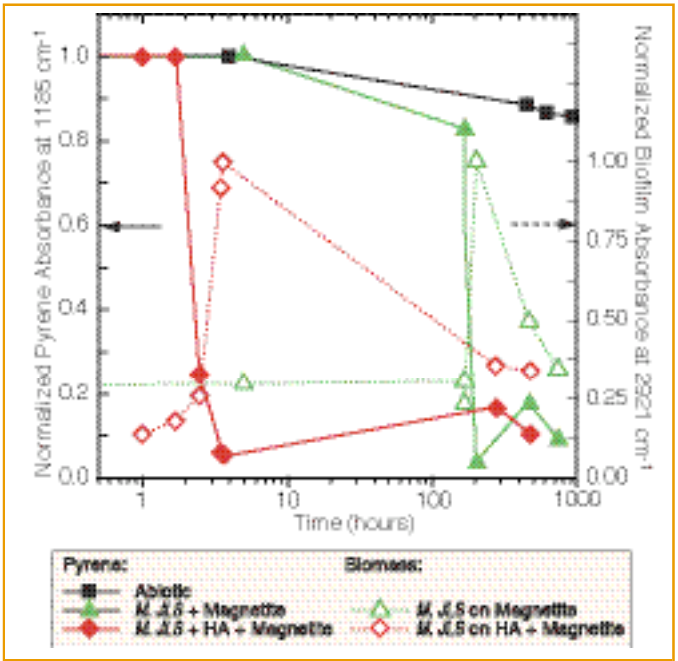


Figure 1. Summary of IR results showing that pyrene degradation occurs much faster when HA is present (note the log scale on the time axis). The color scheme is black for abiotic, green for biotic without HA, and red for biotic with HA. The solid lines show the pyrene amount (*left axis*) as a function of time for each experiment. The dotted lines show a subsequent increase in *Mycobacterium* sp. JLS biomass (*right axis*) after pyrene degradation.

SIGNIFICANCE OF FINDINGS

This is the first study that provides direct evidence that HA can accelerate PAH biodegradation through the mechanism of enhanced bioavailability, which will have significant implications for bioremediation of contaminated soils. We can obtain this type of important biogeochemical information because of our novel and powerful SIR spectromicroscopy technique. This technique enabled research to assess, in real time, the interactions between multiple constituents in contaminated soils.

RELATED PUBLICATION

Holman, H.-Y. N., K. Nieman, D.L. Sorensen, C.D. Miller, M.C. Martin, T. Borch, W.R. McKinney, and R.C. Sims, Catalysis of PAH biodegradation by humic acid shown in synchrotron infrared studies. Environmental Science & Technology, 36(6), 1276–1280, 2002.

ACKNOWLEDGMENTS

This work was partly supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Application of Thermally Enhanced Vapor Extraction at Berkeley Lab

Iraj Javandel and Barry Freifeld
Contact: Iraj Javandel, 510/486-6106, ijavandel@lbl.gov

OBJECTIVE

A plume of contaminated groundwater was found near the site of the first Berkeley Lab cyclotron. Detailed investigations have identified the source area and determined the vertical and lateral extent of the contamination in the subsurface. The contaminants are chlorinated hydrocarbons consisting mainly of perchloroethene, trichloroethene, and carbon tetrachloride. The source area is located within heterogeneous geological materials consisting of both volcanic and sedimentary rocks. The hydraulic conductivity of these materials varies between 10^{-5} and 10^{-9} m/s. Various technologies are being tested to study their applicability for cleaning the source area. The objective of this study was to examine the effectiveness of thermally enhanced vapor extraction in removing contaminants from the source area.

APPROACH

In a pilot-scale test, we used a combination of soil heating and vapor extraction techniques to remove the chlorinated hydrocarbons from very-low-permeability geological materials of the source area. Three heaters, each of approximately 5.3 kilowatts capacity, were placed in three wells at 20 to 40 ft depth. Heater wells were drilled 6 ft apart, at the apexes of an equilateral triangle. Resistive heating raised soil temperature to a maximum of 200°C. Both liquid and vapor were extracted from a well at the center of the triangle. Two instrumented wells were installed within 5 ft of one of the heaters. Temperatures were measured along the heater well casings, the extraction well, and at various depths in the instrumented wells. In addition, soil gas probes and vacuum lysimeters were installed at various depths in the instrument wells. Soil vapor and soil water from all sampling points were collected and tested periodically, while flow rate and chemical composition of soil gas samples collected at the top of the extraction well were measured. The test continued for about 18 months.

ACCOMPLISHMENTS

More than 500 kg of perchloroethene, trichloroethene, and carbon tetrachloride were removed from the source area. This estimate is based on the measured flow rates and concentrations of contaminants in the extracted air. Note that the total mass of dissolved chlorinated hydrocarbons in the groundwater plume before this experiment was estimated to be about 7 kilograms.

SIGNIFICANCE OF FINDINGS

- Thermally enhanced vapor extraction proves to be an excellent technique for removing dispersed nonaqueous-phase liquids from very-low-permeability heterogeneous geological materials.
- If the test were not properly designed, some of the chemicals volatilized may diffuse and condense into areas that were previously clean.

ACKNOWLEDGMENTS

This work is part of Berkeley Lab's Environmental Restoration Program, supported by the DOE Office of Environmental Management, under U.S. Department of Energy Contract No. DE-AC03-76SF00098.

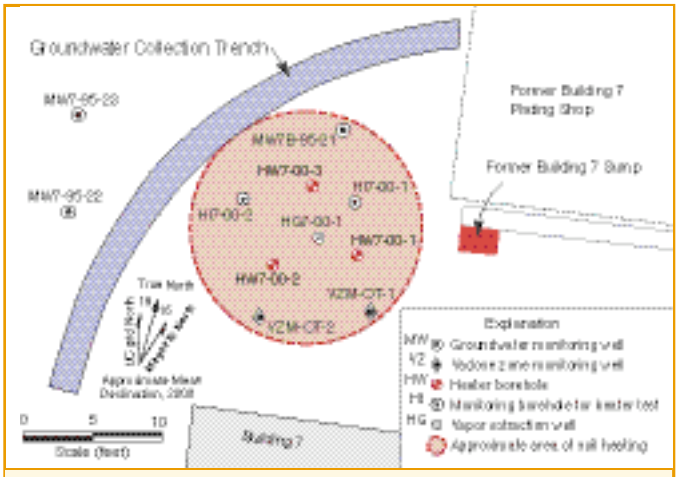


Figure 1. Location of thermally enhanced vapor extraction pilot test.

High-Frequency Electromagnetic Impedance Measurements for Characterization, Monitoring, and Verification Efforts

Ki Ha Lee, Alex Becker, and Hung-Wen Tseng
Contact: Ki Ha Lee, 510/486-7468, khlee@lbl.gov

RESEARCH OBJECTIVES

Noninvasive, high-resolution imaging of the shallow subsurface is needed for delineation of buried waste, detection of unexploded ordinance, verification and monitoring of containment structures, and other environmental applications. Electromagnetic (EM) measurements at frequencies between 1 and 100 MHz are important for such applications, because the induction number of many targets is small and the ability to determine the dielectric constant (in addition to the electrical conductivity) of the subsurface is possible. Earlier investigators were successful in developing systems for detecting anomalous areas, but no quantifiable information was accurately determined. For high-resolution imaging, accurate measurements are necessary, so that field data can be mapped into the space of the subsurface parameters. The objective of this project is to develop a noninvasive method for accurately mapping the electrical conductivity and dielectric constant of the shallow subsurface, using the EM impedance.

APPROACH

EM impedance, the ratio of electric to magnetic field, can be used to map subsurface electrical properties without the exact knowledge of the transmitter signal. A prototype 30 MHz high-frequency impedance (HFI) system was originally assembled using off-the-shelf components, including a magnetic dipole transmitter as well as electric and magnetic antennae. The system was tested in known areas against theoretical predictions (Lee and Becker, 2001), thereby verifying the utility of the EM impedance for shallow subsurface application. The test was focused on mapping only the electrical conductivity because the frequency was limited to 30 MHz. To improve data quality and to include the capability of mapping dielectric constants, we began modifying the HFI system by miniaturizing the transmitter and receiver electronics and implementing fiber optics communication.

ACCOMPLISHMENTS

Success in achieving the overall objective of the HFI system depends on the accuracy of field measurements, especially in the electric field. All electronic components have been miniaturized and repackaged, and communication is now done via optical fibers. The other important improvement for the acquisition system has been the replacement of the lock-in amplifier with the HP network analyzer. This allows much wider operating bandwidth for the HFI system, well beyond 100 MHz with greatly improved efficiency (Lee et al., 2002). Along with the hardware, we developed a one-dimensional inversion scheme, INVEM1D, in which the electrical conductivity and dielectric constant of an N-layered earth are simultaneously inverted. The key development has been the successful implementation of the analytically evaluated sensitivity function to the inversion code.

SIGNIFICANCE OF FINDINGS

The improved HFI system can be used to map shallow subsurface electrical conductivity and the dielectric constant simultaneously.

RELATED PUBLICATIONS

Lee, K.H., and A. Becker, High-frequency electromagnetic impedance measurements for characterization, monitoring and verification efforts. Interim Report, Project #60328, U.S. DOE, 2001.

Lee, K.H., A. Becker, and H.-W. Tseng, High-frequency electromagnetic impedance measurements for characterization, monitoring and verification efforts. Annual Report, Project #73776, U.S. DOE, 2002.

ACKNOWLEDGMENTS

This work was supported by the Assistant Secretary of the Office of Environmental Management, Office of Science and Technology, Environmental Management Science Program, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

The Role of Biogeochemical Dynamics in the Formation of U(VI) Solid Phases

Tracy E. Letain, Terry C. Hazen, and Heino Nitsche
Contact: Tracy E. Letain, 510/486-6612, teletain@lbl.gov

RESEARCH OBJECTIVES

To assist the U.S. Department of Energy with long-term stewardship issues associated with bioremediation of uranium (U), we seek to define the mechanisms by which microorganisms facilitate the formation of U(VI) solid phases. Under anaerobic conditions, microbial reduction of U(VI) to U(IV) can potentially decrease groundwater U contamination by lowering solubility and by slowing migration through the soil. However, such biological alteration must be considered temporary unless long-term anaerobicity can be maintained. When aerobic conditions return, U(IV) will likely re-oxidize to U(VI), which is generally more soluble and potentially more mobile. The transformation to U(VI)-phosphate solids is of particular interest, since the U(VI) phosphates are the least soluble of the U(VI) solids found in nature.

APPROACH

Bacteria present in soils may play a role in the formation of U(VI)-phosphate solid phases, both because they serve as an available phosphate source and because the cell surface may act as a nucleation site for the reprecipitation of U. We are investigating the ability of some model microorganisms, such as the Gram-positive bacterium, *Bacillus sphaericus*, to complex with U(VI). Ability of *B. sphaericus* to sorb U(VI) has been tested for a wide pH range (pH 3–pH 7), with special attention to the sorption behavior at low concentrations of U, such as would be commonly found in contaminated waste sites. The cell surface group responsible for U(VI) complexation is identified by both laser-induced fluorescence spectroscopy (LiFS) and x-ray absorption spectroscopy (XAS).

ACCOMPLISHMENTS

We find *B. sphaericus* can remove even trace amounts of U(VI) from solution (to below the detection limit of 10-8 moles/L U(VI). Isotherm modeling of U(VI) sorbed onto *B. sphaericus* at pH 5 suggests the presence of greater than one bacterial cell surface site available for U complexation. Both LiFS and XAS yield data that are consistent with the cell surface organic phosphate functional group, called teichoic acid, being the dominant site for U(VI) complexation. U(VI) sorption by *B. sphaericus* is somewhat pH-dependent, with U(VI) sorption capacity increasing initially with increasing pH (from pH 3 to pH 5), and similar sorption capacity seen for pH 5–7.

SIGNIFICANCE OF FINDINGS

Up to this time, no other group has been able to determine U(VI) sorption onto bacteria at the very low and environmentally relevant concentrations of both U(VI) and bacteria used in this study (over 100-fold lower than previous studies). We are the only group testing U(VI) sorption at pH values greater than 5, partly due to the low solublity of U(VI) at higher pH values. Additionally, using a combination of LiFS and XAS to determine the cell surface functional group has led to the strongest evidence to date of organic phosphate serving as the dominant group responsible for U(VI) complexation.

RELATED PUBLICATIONS

Letain, T.E., J.A. Warner, D.K. Shuh, and H. Nitsche, EXAFS study of pH-dependent uranyl adsorption to bacteria. In preparation for Geochimica et Cosmochimica Acta, 2003.

Letain, T.E., T.C. Hazen, and H. Nitsche, *Bacillus sphaericus* surface interactions with uranium (VI) at environmentally relevant concentrations. Appl. Environ. Microbiol., 2003 (submitted).

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Natural and Accelerated Bioremediation Research Program, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Use of Sr Isotopes to Determine Long-Term Average Vadose Zone Infiltration Flux at Hanford 200W Area

Katharine Maher, Donald J. DePaolo, and Mark S. Conrad
Contact: Katharine Maher, 510/642-9524, kmaher@eps.berkeley.edu

RESEARCH OBJECTIVES

Infiltration rates are an important variable in assessing contaminant transport at the Hanford Site, where the majority of the contaminants are contained in the upper 30 m of a thick (~70 m) vadose zone. The transit time to the aquifer for a given contaminant largely determines the remediation action, especially for mobile radioactive contaminants. Efforts to quantify infiltration rates at the Hanford Site have been hindered by the complexity of the hydrogeologic setting, the thick vadose zone, and recent anthropogenic disturbances. Independent estimates of infiltration rates range from 0.01 mm/yr to 200 mm/yr, depending on the method and surface cover.

Using variations in the natural strontium (Sr) isotopic compositions of vadose zone pore waters and sediments, the infiltration flux can be quantified using a simple one-dimensional reactive transport model. The strontium isotope ratio ($^{87}Sr/^{86}Sr$) of pore water is a very sensitive indicator of interaction with the rock matrix. Because of the relatively low concentration of Sr in the pore water relative to the sediments, even minor exchange between the solid and fluid phases will quickly shift the pore-water Sr isotope ratio towards that of the rock. The pore water $^{87}Sr/^{86}Sr$ value is thus controlled by a balance between the infiltration flux and weathering of the sediments.

APPROACH

Strontium isotope ratios were measured in the pore water, acid extracts, mineral separates, and sediments of a 70 m vadose zone core in the 200W Area of the Hanford/DOE complex in eastern Washington State. Using an estimate of the bulk weathering rate for the sediments, the steady-state reactive transport model for Sr in the vadose zone was inverted to solve for the infiltration rate (see Maher et al., 2003). This method is currently being applied to other locations around the Hanford Site.

ACCOMPLISHMENTS

Given a range of weathering rates based on sediment mineralogy, the infiltration flux for the 200W Area is constrained at between 7 ± 3 mm/yr (Figure 1). Non-steady-state models spanning the last 15 kyr reveal that the profile is very close to steady state; therefore, these infiltration flux values are applicable over at least this time span. The transit time for meteoric water to percolate from surface to the water table is in the range of ~1,200 years.

SIGNIFICANCE OF FINDINGS

The method of inferring infiltration rates using Sr isotopes provides a novel method for quantifying fluid flow in the vadose zone. This method is advantageous in that it does not require disturbance of the site prior to measurement (e.g., lysimeters), it does not rely *ab initio* on assumptions regarding atmospheric and geochemical parameters (e.g., Cl mass balance), it can be applied to deep heterogeneous vadose zones, and it provides a long-term (~1–10 kyr) average of the infiltration flux.

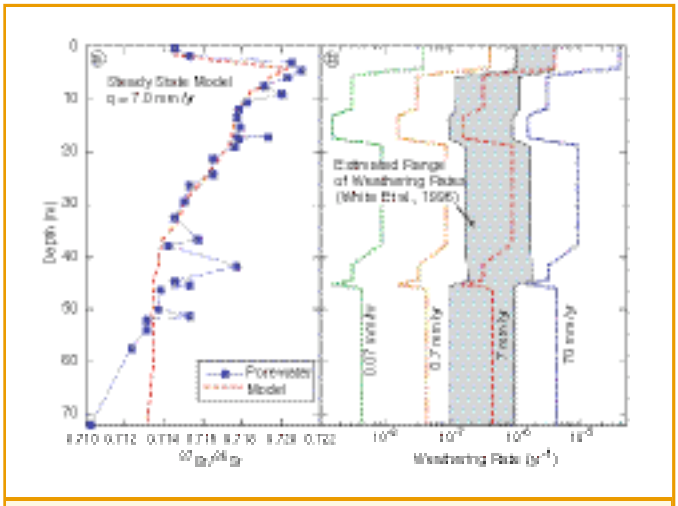


Figure 1. Steady-state model best-fit trajectory and weathering rate profile: (a) the $^{87}Sr/^{86}Sr$ values for the pore waters decrease systematically with depth, from a high value of 0.721 near the surface towards the bulk sediment average value of 0.711; (b) weathering rates required to fit the data for various infiltration rates, and the range of estimated rates based on soils data from White et al. (1996). The models suggest that the infiltration flux for the site is 5 to 10 mm/yr. The method shows potential for providing long-term *in situ* estimates of infiltration rates for deep heterogeneous vadose zones.

RELATED PUBLICATIONS

Maher, K., D.J. DePaolo, and M.E. Conrad, Vadose zone infiltration rate at Hanford, Washington, inferred from Sr isotope measurements. Water Resources Research 39 (8), 1204, 2003.

DePaolo, D.J., M.E. Conrad, and K. Maher, Oxygen and hydrogen isotopes in pore fluids from a 70 m thick vadose zone. Vadose Zone Journal, 2003 (submitted).

ACKNOWLEDGMENTS

Funding was provided by the Department of Energy under Contract No. DE-AC06-76RL01830 through the Hanford Science and Technology Program, and by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Simulating Landfill Biodegradation Processes with T2LBM

Curtis M. Oldenburg, Sharon E. Borglin, and Terry C. Hazen
Contact: Curtis M. Oldenburg, 510/486-7419, cmoldenburg@lbl.gov

RESEARCH OBJECTIVES

We have developed T2LBM, a module for the TOUGH2 simulator that implements a Landfill Bioreactor Model. This model can simulate processes of aerobic or anaerobic biodegradation of municipal solid waste (MSW) and the associated flow and transport of gas and liquid. We present an example study to verify the code against a laboratory experiment carried out in a parallel effort. The overall objective of our MSW landfill research is to investigate the advantages and disadvantages of different landfill treatment approaches.

APPROACH

We have enhanced an existing numerical reservoir simulator to include additional chemical components and biodegradation processes relevant to MSW. Our approach assumes that a single substrate component (acetic acid, CH_3COOH) serves as a proxy for all of the biodegradable fractions in MSW. T2LBM includes six chemical components (H_2O, CH_3COOH, CO_2, CH_4, O_2, N_2) and heat distributed in gaseous and aqueous phases with partitioning by Henry's law. This approach further assumes, implicitly, that hydrolysis reactions occur to produce acetic acid. Gas and liquid containing the chemical components flow through the MSW refuse mass as governed by Darcy's law. The focus of the process model is on biodegradation with nonisothermal effects and the associated gas production, along with liquid- and gas-phase flow through the refuse mass.

ACCOMPLISHMENTS

We have carried out tests of T2LBM and compared results against published studies of biodegradation. In addition, we have compared T2LBM results to the laboratory experiment of MSW biodegradation carried out in parallel with model development. Shown in Figure 1 are the volume fractions of oxygen (O_2) from the experiment and from a T2LBM simulation over a 40-day period. The event being examined is a respiration test in a system where air is blown into the MSW for 28 days to keep it aerobic, and then (for a short period) the air is turned off and the system is shut in. Over the period of shut in, we can observe the rate of O_2 consumption, i.e., respiration. During the shut-in period, the O_2 was rapidly consumed, and the system became anaerobic. At t = 31 days, the fan was turned back on, air addition continued, and the system became aerobic again. As shown in Figure 1, T2LBM was able to match the observed O_2 volume fraction data fairly well, using kinetic biodegradation parameters from the literature. We also plot the T2LBM CO_2 curve to show its relation to the transition from aerobic to anaerobic conditions.

SIGNIFICANCE OF FINDINGS

Our preliminary testing of T2LBM suggests that the simulator is capable of modeling fundamental aspects of MSW biodegradation processes. Further development and testing are needed to elucidate the capabilities and limitations of the model for simulating laboratory experiments and actual MSW landfills.

RELATED PUBLICATION

Oldenburg, C.M., T2LBM: Landfill Bioreactor Model for TOUGH2, Version 1.0. Berkeley Lab Report LBNL-47961, 2001.

ACKNOWLEDGMENTS

This work was supported by Laboratory Directed Research and Development (LDRD) funding from Berkeley Lab, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

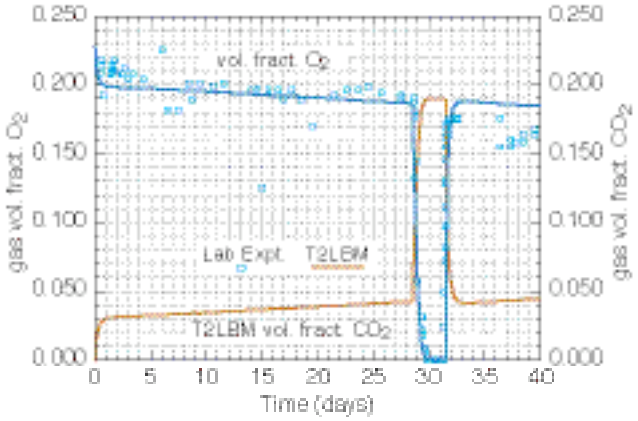


Figure 1. Volume fractions of O_2 from the laboratory experiment and from T2LBM plotted along with volume fraction of CO_2 from T2LBM

TMVOC, A Simulator for Multiple Volatile Organic Chemicals

Karsten Pruess and Alfredo Battistelli[1]
[1]Aquater S.p.A., Italy
Contact: Karsten Pruess, 510/486-6732, k_pruess@lbl.gov

RESEARCH OBJECTIVES

Many environmental contamination problems involve volatile organic chemicals (VOCs), such as crude oil, gasoline, diesel, and/or organic solvents. When spilled into the unsaturated zone, these chemicals may form a separate nonaqueous phase, giving rise to three-phase flow of water, soil gas, and a nonaqueous phase liquid (NAPL). Such flows can be modeled with T2VOC, but that code is limited to conditions in which the VOC is a pure, single-component fluid. However, in many cases of interest, nonaqueous fluids released into the subsurface may consist of a multicomponent mixture of several different chemicals. TMVOC is designed for three-phase flows in which the NAPL consists of a general multicomponent mixture of organic fluids. In addition, one or several noncondensable gases (NCGs) may be present.

APPROACH

TMVOC is based on the M2NOTS code that was developed by Adenekan (1992) as part of his Ph.D. project at the University of California, Berkeley. It is implemented as a specialized module for Berkeley Lab's general multipurpose simulator TOUGH2 and retains its general process-modeling capabilities and user features.

ACCOMPLISHMENTS

In the TMVOC formulation, the multiphase system is assumed to be composed of water, NCGs, and water-soluble VOCs. The number and nature of NCGs and VOCs can be specified by the user. Organic chemicals with critical temperatures below ambient, such as methane or ethane, can be modeled as NCGs. There are no intrinsic limitations to the number of NCGs or VOCs. Thermophysical property data for individual VOCs must be provided by the user. TMVOC uses a very general formulation to obtain thermophysical and PVT (pressure-volume-temperature) properties for mixtures of VOCs and NCGs. The fluid components may partition (volatilize and/or dissolve) among gas, aqueous, and NAPL phases. Any combination of the three phases may be present, and phases may appear and disappear in the course of a simulation.

Flows can be nonisothermal, and may involve advective, diffusive, phase-partitioning, and sorptive processes. A simple model for biodegradation is provided as well. Chief applications for which TMVOC is designed include analysis of NAPL spills and remediation alternatives in the vadose zone and below the water table.

A detailed self-contained user's guide is available that provides a technical reference to the TMVOC formulation and includes seven sample problems to illustrate code applications:

1. Demonstrating initialization of different phase conditions
2. One-dimensional Buckley-Leverett flow
3. Diffusion
4. Steam displacement of TCE
5. Steam displacement of a benzene-toluene mixture
6. Air displacement of NAPL
7. NAPL spill in the unsaturated zone

TMVOC is upwardly compatible with T2VOC; that is, T2VOC input files can be executed with TMVOC.

SIGNIFICANCE OF FINDINGS

The TMVOC code is available through DOE's Energy Science and Technology Software Center (see http://www-esd.lbl.gov/TOUGH2/tmvoc.html).

RELATED PUBLICATIONS

Adenekan, A.E., Numerical modeling of multiphase transport of multicomponent organic contaminants and heat in the subsurface. PhD thesis, University of California at Berkeley, 1992.

Pruess, K. and A. Battistelli. TMVOC, a numerical simulator for three-phase non-isothermal flows of multicomponent hydrocarbon mixtures in saturated-unsaturated heterogeneous media. Berkeley Lab Report LBNL-49375, 2002.

ACKNOWLEDGMENTS

This work was supported, in part, by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Partial support was also provided by a grant from Aquater S.p.A. (ENI Group) to Berkeley Lab in the frame of the REPIS project, sponsored by the ENI Research Fund.

Real-Time Management of Dissolved Oxygen in the San Joaquin River Deep-Water Ship Channel

Nigel W.T. Quinn, William T. Stringfellow, and Jeremy Hanlon
Contact: Nigel W.T. Quinn, 510/486-7056, nwquinn@lbl.gov

RESEARCH OBJECTIVES

A decision support system (DSS) is under development within ESD as part of a CALFED-sponsored project to assist in management of episodes of low-dissolved-oxygen concentrations in the San Joaquin River (SJR) Deep-Water Ship Channel (DWSC). Biodegrading algae and organic sediments that settle in the DWSC remove oxygen from the water column. When dissolved oxygen concentrations dip below 5 mg/L, conditions adverse to the survival of juvenile salmon arise. ESD's science role in this project to date has been to develop an understanding of the relative algal contributions made by agriculture and managed seasonal wetlands, the fate of this algae in transit along the SJR, and its impact on dissolved oxygen in the DWSC.

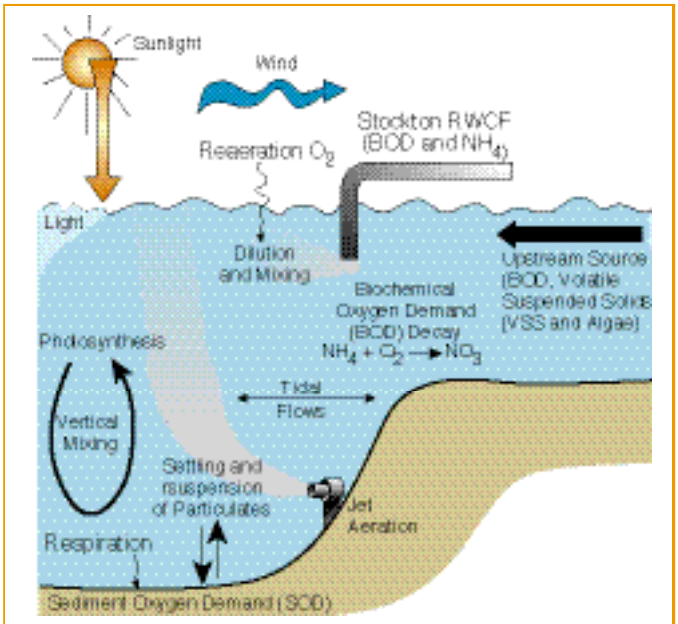


Figure 1. Conceptual model of factors contributing to low dissolved levels in the Stockton Deep-Water Ship Channel

APPROACH

Flow and water quality were measured at three paired stations to obtain representative total biochemical oxygen demand (BOD), carbonaceous biochemical oxygen demand (CBOD), and nitrogenous biochemical oxygen demand (NBOD) estimates for agricultural sources, privately owned wetlands, and public refuges. Total organic carbon (TOC), dissolved organic carbon (DOC), total suspended solids (TSS) and volatile suspended solids (VSS) were measured at each of the paired sites to further discriminate between the origin of the carbon that exerted the carbonaceous BOD. Ammonia, total phosphorous, and ortho-phosphate were also measured to determine the importance of these nutrients in potentially limiting the biodegradation rates of carbonaceous material. Chlorophyll *a* concentrations provided an estimate of algae concentrations at each of the sites. Algae loads were compared for each upstream and downstream paired site to determine algal growth rates within each of these major drainage conveyances to the SJR. These findings were used to complete a conceptual model of upper-watershed algal loading to the DWSC.

ACCOMPLISHMENTS

The major west-side drainage conveyances, Mud Slough and Salt Slough, were shown to contribute approximately 35% of the BOD entering the SJR. This suggests that algal growth in the SJR and east-side drainage contributions are more important than previously suspected in their contribution to DWSC dissolved-oxygen deficits. In the Mud Slough sub-basin, we were able to differentiate drainage coming from managed wetlands and agricultural land. Our research also confirmed the importance of irrigation diversions in affecting algal loading to the DWSC. Sharp reductions in agricultural diversions at both water districts increased algal loading to the DWSC during the months of September and October, and coincided with reduced dissolved-oxygen levels starting in mid-October, suggesting a possible causal mechanism.

SIGNIFICANCE OF FINDINGS

This study has identified a possible opportunity to reduce the amount of oxygen-demanding materials entering the SJR from this watershed. The conceptual model developed and tested in this investigation will assist in calibration of a hydrodynamic water quality model of the SJR and its contributing watersheds. This model will form the basis of a DSS to forecast and help manage dissolved-oxygen levels in the DWSC.

RELATED PUBLICATIONS

Quinn, N.W.T and A.T. Tulloch, San Joaquin River diversion data assimilation, drainage estimation and installation of diversion monitoring stations. Final Report. CALFED Bay-Delta Program, Sacramento, California, pp. 211, 2002.

Stringfellow, W.T., and N.W.T. Quinn. 2002. Discriminating between west-side sources of nutrients and organic carbon contributing to algal growth and oxygen demand in the San Joaquin River. CALFED Bay-Delta Program, Sacramento, California, 2002; Berkeley Lab Report No. LBNL-51166, 2002.

ACKNOWLEDGMENTS

The authors wish to thanks the CALFED Bay-Delta Program for funding the research and to their fellow scientists on the Technical Advisory Committee, who provided valuable review of our work.

Biological Treatment of Mixed Wastes: A Safer Alternative to Incineration

William T. Stringfellow, Tatsuyuki Komada, and Li-Yang Chang
Contact: Will Stringfellow, 510/486-7903, wstringfellow@lbl.gov

RESEARCH OBJECTIVES

The objective of this research was to develop a biological treatment process that could serve as an alternative to incineration for the treatment of mixed wastes. Mixed wastes are wastes that contain both radioactive materials and hazardous chemicals. Radioactive wastes are regulated under the Atomic Energy Act and are most safely disposed of in a secure landfill where the radioactivity is excluded from the biosphere. Hazardous wastes are regulated under the Resource Conservation and Recovery Act (RCRA) and are prohibited from disposal in landfills. Hazardous waste regulations take priority, and mixed wastes are typically incinerated. During incineration, radioactivity is released directly to the biosphere.

The advantage of biological treatment is that radioactivity can be contained during treatment of the hazardous waste component. Once the hazardous waste component is treated biologically, the waste is no longer regulated under RCRA, and the radioactivity can be kept from the biosphere.

APPROACH

To meet the objective of a completely contained treatment process, we developed a "Drip-Feed Bioreactor" (Figure 1). Unlike conventional biological treatment systems, in the drip-feed system the waste stream flows into the reactor, but no waste flows out. In the reactor, the waste is contacted with specially prepared bacterial cultures that completely destroy the hazardous waste to carbon dioxide and water. The radioactive waste is not treated by the bacteria, but is contained in the reactor for recovery and safe disposal.

ACCOMPLISHMENTS

The Drip-Feed Bioreactor was tested for the treatment of a mixed waste containing acetonitrile (the hazardous waste) and tritium (the radioactive waste). This type of waste is generated during biomedical research at universities and hospitals throughout the nation. Under the RCRA regulations, the acetonitrile must be reduced to below 1.0 mg/L before the waste is no longer considered hazardous. A surrogate (nonradioactive) waste was tested that contained acetonitrile at a concentration of approximately 10% by volume. Results of this trial are as follows: influent acetonitrile concentration, 88,000 mg/L; final acetonitrile concentration, less than 0.1 mg/L.

SIGNIFICANCE OF FINDINGS

This study demonstrated that the Drip-Feed Bioreactor could be used to treat mixed wastes containing acetonitrile to concentrations below 1.0 mg/L, the land disposal restriction for this compound. This study showed that mixed wastes can be treated without releasing radioactivity and that incineration should not be considered the only alternative for treatment of mixed wastes.

This study represents the first time that a highly concentrated hazardous waste has successfully been treated biologically without excessive dilution. The robust nature of the Drip-Feed Bioreactor suggests that this reactor could be used to treat other concentrated hazardous or toxic wastes, including scintillation cocktail and chemical agents.

RELATED PUBLICATION

Chang, L.-Y., A. Proctor, and W.T. Stringfellow, Kinetic parameters for the biological treatment of mixed wastes containing acetonitrile and methanol. Berkeley Lab Formal Report LBID-2433, 2002.

ACKNOWLEDGMENTS

This project was partially supported by the Assistant Secretary of the Office of Environmental Management (EM) and Office of Science (OS) through Department of Energy Contract No. DE-AC03-76SF00098. The High Pressure Liquid Chromatography (HPLC) waste compositions were kindly provided by Dr. Philip Williams and Chit Than of the National Tritium Labeling Facility of Berkeley Lab. This research was also partially supported by the Center for Science and Engineering Education at Berkeley Lab. Special thanks to Jeremy Hanlon for his assistance on this project.

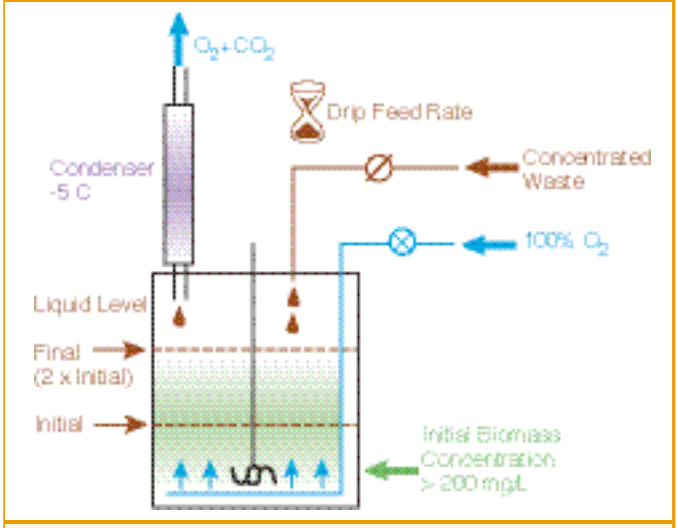


Figure 1. Drip-feed bioreactor schematic

Estimates of Hydraulic Conductivities Along the Russian River Using Groundwater Temperature Profiles

Grace W. Su, James Jasperse[1], Donald Seymour[1], and Jim Constantz[2]
[1]Sonoma County Water Agency, Santa Rosa, CA, 95406
[2]U.S. Geological Survey, Menlo Park, CA, 94025
Contact: Grace Su, 510/495-2338, gwsu@lbl.gov

RESEARCH OBJECTIVES

Quantifying surface-groundwater exchanges has become an important component of water resources management, resulting from the increase in the conjunctive use of water resources. Reducing uncertainty in models used to select optimal operation management alternatives requires proper identification of the spatial and temporal variations in physical parameters, such as the hydraulic conductivity.

Recently, heat as a tracer has been demonstrated to be a robust method for quantifying surface-groundwater exchanges. Groundwater temperatures and water levels are routinely monitored in observation wells near streams, but temperature data are generally considered a water-quality parameter and are not used as an environmental tracer to characterize hydraulic parameters. The objective of this study is to quantify the spatial and temporal variations of the alluvial aquifer hydraulic conductivites along the middle reaches of the Russian River in Sonoma County, California, by analyzing groundwater temperature profiles and water levels measured in six observation wells.

APPROACH

Stream temperatures, groundwater temperatures, and well water levels recorded from June 2000 through October 2000 were used to develop two-dimensional groundwater flow and heat transport simulations of the region from the river to each observation well. Different values for the hydraulic conductivity were used in the simulations, and the value resulting in the smallest difference between the simulated and observed temperatures was considered the best estimate. Simulations were performed under isotropic conditions and with anisotropy (horizontal-to-vertical hydraulic conductivity) values of 2 and 5.

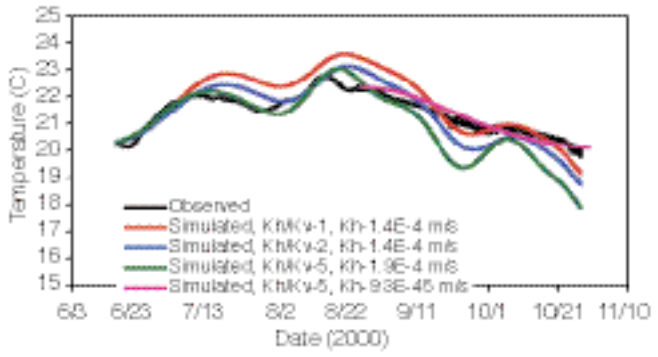


Figure 1. Groundwater temperatures recorded between June and October 2000 in an observation well close to a dam and the best fit simulated temperature profiles at different anisotropies (Kh/Kv). After mid-August, a smaller conductivity is necessary to obtain a good fit.

ACCOMPLISHMENTS

Estimated hydraulic conductivities varied by almost two orders of magnitude over the six locations analyzed, from 1.7 × 10^{-5} m/s to 2.3 × 10^{-3} m/s. The simulated temperature profiles generally fit the observed ones best when an anisotropy of 5 was used. In some locations, a change in the observed temperature profile occurred through the summer and fall, most likely caused by deposition of fine-grained sediment and organic matter plugging the streambed. A reasonable fit to this change in the temperature profile was obtained by decreasing the hydraulic conductivity in the simulations. The most significant decrease in conductivity occurred in the region closest to an inflatable dam, where the conductivity decreased by about one-half after mid-August, as shown in Figure 1.

SIGNIFICANCE OF FINDINGS

The results of this study demonstrate that groundwater temperatures and water levels monitored in observation wells can provide an effective means of estimating alluvial aquifer hydraulic conductivities. The temporal and spatial estimates in hydraulic conductivities will be incorporated into a three-dimensional groundwater model of this study area currently under development.

RELATED PUBLICATION

Su, G.,W., J. Jasperse, D. Seymour, and J. Constantz, Analysis of water levels and temperatures in wells to estimate alluvial aquifer hydraulic conductivities. Ground Water, 2003 (submitted).

ACKNOWLEDGMENTS

This work was supported by the Sonoma County Water Agency (SCWA), through U.S. Department of Energy Contract No. DE-AC03-76SF00098.

Unsaturated Hydraulic Properties of Gravels

Tetsu K. Tokunaga, Keith R. Olson, and Jiamin Wan
Contact: Tetsu Tokunaga, 510/486-7176, tktokunaga@lbl.gov

RESEARCH OBJECTIVES

Gravels can make up large fractions of the subsurface, including vadose zones. The extensiveness of some gravel deposits is evident from the fact that they serve as major aquifers that supply groundwater for agricultural, industrial, and municipal use. Because some gravel deposits do occur in the vadose zone, understanding unsaturated flow and transport in such settings requires knowledge of their hydraulic properties. Some gravel deposits occur in heavily contaminated vadose zones such as the Hanford Site in Washington State, where radioactive wastes have leaked. Gravels are also an important component in engineered capillary barriers for subsurface waste isolation. However, relatively little information is available on the unsaturated hydraulic properties of gravels. In a recent study (Tokunaga et al., 2002), the levels of residual saturation in Hanford gravels were found to be high, in the range of 0.1 to 0.2. The present work addresses a much broader range of matric (capillary) potentials and saturations in Hanford gravels, and includes characterization of intragranular porosity and water film thicknesses on external grain surfaces.

APPROACH

To cover a wide range of matric potentials (0 to -300 MPa), water-retention measurements were made using suction plate, pressure plate, and vapor-pressure methods (Figure 1). Average water film thicknesses on external surfaces of gravel grains were obtained with a synchrotron x-ray microprobe-based suction plate technique (Tokunaga et al., 2003). External grain surfaces were also characterized with a laser profilometer, atomic force microscope, and scanning electron microscope. Intragranular surface area was determined with adsorption isotherms (water vapor and krypton gas).

ACCOMPLISHMENTS

External surfaces of these gravels have root mean-square roughnesses in the μm range, with sparsely distributed deep (hundreds of μm) pits. Water films on these external surfaces are volumetrically insignificant at matric potentials less than about -2 kPa. Residual water in these gravels occurs in intragranular pores, accounts for about 10% of the total porosity, and is effectively hydraulically immobile. The insignificant advective access to this intragranular domain was established from measurements that show less than 2% change in saturation over the matric potential interval of -10 kPa to -10 MPa. The intragranular domain in Hanford gravels also has a large specific surface area of about 11 $m^2\ g^{-1}$.

SIGNIFICANCE OF FINDINGS

The high specific surface area and porosity associated with interior regions of Hanford gravel grains largely explain why exchanges of solutes (including contaminants) in these sediments are significant and strongly diffusion-limited.

RELATED PUBLICATIONS

Tokunaga, T.K., J. Wan, and K.R. Olson, Saturation-matric potential relations in gravel. Water Resour. Res. 38(10), 1214, doi:10.1029/2001WR001242, 2002.

Tokunaga, T.K., K.R. Olson, and J. Wan, Moisture characteristics of Hanford gravels: Bulk, grain-surface, and intragranular components. Vadose Zone J. accepted June 2, 2003.

ACKNOWLEDGMENTS

This project is supported by the Assistant Secretary of the Office of Environmental Management, Office of Science and Technology, of the U.S. Department of Energy under Contract No. DE-AC03-76-SF00098.

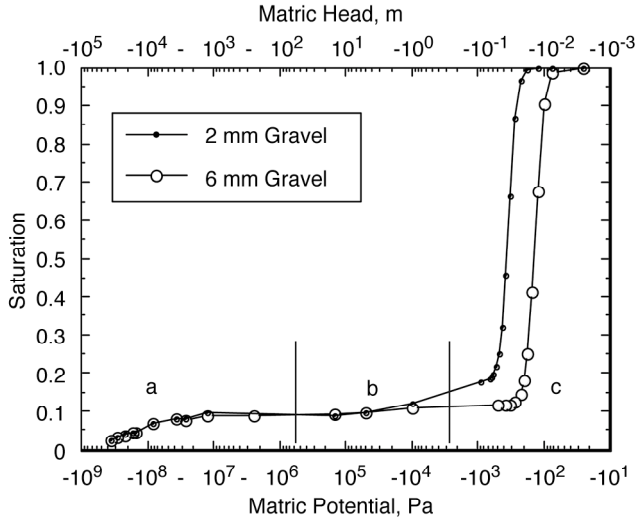


Figure 1. Moisture retention in 2 and 6 mm Hanford gravels, over a wide range of matric (water) potentials. Measurement methods used are indicated along the x-axis as (a) vapor-pressure regulation, (b) pressure plate, and (c) suction plate. The vapor-pressure equilibration region data were obtained in adsorption mode. The suction plate and pressure plate data were obtained in drainage mode.

Bioprospecting in Extreme Environments

Tamas Torok, Center for Environmental Biotechnology
Contact: 510/486-5808 ttorok@lbl.gov)

RESEARCH OBJECTIVES AND SIGNIFICANCE

Extremophilic microorganisms are adapted to survive in such ecological niches as high temperatures, extremes of pH, high salt concentrations, and high pressures. Therefore, extremophilic microorganisms represent a challenging scientific opportunity, not only for those interested in microbial diversity and the evolution of life, but for researchers searching for clues to extraterrestrial life. Also, extremophiles produce unique biocatalysts that function under extreme conditions comparable to those prevailing in various industrial processes. Bioprospecting for extremophiles with potential immediate use in the food, chemical, and pharmaceutical industries—and in environmental biotechnology—is therefore highly relevant.

In fulfilling the national security and biological nonproliferation missions of the U.S. Department of Energy, the main objective of this research is to establish a multiyear bioprospecting program for novel biotechnology applications in the extreme environments of the Newly Independent States (NIS) of the former Soviet Union. In previous years, the program collected environmental samples in the exclusion zone of the failed nuclear power plant in Chernobyl, around Lake Baikal in Siberia, and on the Kamchatka peninsula. Currently, we are expanding our research to the deserts and hot springs in Uzbekistan, the Caucasus mountain sites in Georgia, and the former nuclear test site in Kazakhstan.

APPROACH AND RESULTS

Structure of the microbial community in an ecological niche is characteristic for the ongoing biogeochemical processes. We use a polyphasic approach to microbial community characterization—i.e., both culture-based and alternative, nonculture-based techniques. We have isolated several thousand new microbial strains and detected novel restriction enzymes (as well as unique combinations thereof). Isolated microorganisms are then grown under proprietary, secondary metabolite-producing conditions, and the resulting natural products are screened for innovative crop protection and biomedical application in collaboration with our biotech industry partners. Lead molecules are chemically characterized. Nucleic acid sequences of interest extracted from extreme environmental samples are used in recombinant technologies and lead to novel biocatalysts and biologically active molecules, with a wide range of applications in industry, agriculture, and medicine. Microorganisms and their natural products are being protected by joint patent disclosures. Berkeley Lab is licensing the cultures to the industrial partners. Royalties and other benefits are equitably shared with the NIS researchers.

ACKNOWLEDGMENTS

This program has been supported by DOE's Initiatives for Proliferation Prevention (IPP) program. The author wishes to express his deepest appreciation for the support he received from colleagues at the International Institute of Cell Biology, Kiev, Ukraine; the State Research Center of Virology and Biotechnology, "VECTOR", Koltsovo, Novosibirsk region; the Institute of Volcanology, Petropavlovsk-Kamchatsky, a member of the Far East Branch of the Russian Academy of Sciences (RAS); the Institute of Geochemistry of the RAS, Irkutsk; and the Buryat Institute of Geology in Ulan Ude, Russia. Special thanks are due to the Baikal Drilling Project and the members of the Russian drilling crew for their professional understanding and support. Special thanks are extended to G. Dahlbacka, Berkeley Lab's ILAB representative. Without his active support, this program could not have achieved its goals.

Constant-Head Well Testing in Support of Environmental Remediation

Robert C. Trautz, Iraj Javandel, and Preston D. Jordan
Contact: Rob Trautz, 510/486-7954, rctrautz@lbl.gov

RESEARCH OBJECTIVES

Groundwater contamination resulting from improper waste disposal and accidental releases of chemicals to the environment is a significant problem faced by many communities. Numerous technologies have been developed over the past two decades to treat contaminated groundwater. Selection of the best-available technology for a given site is based on the treatment technology's ability to either remove or immobilize the contaminant and the cost of implementing the treatment. Both criteria are typically evaluated in light of contaminant travel times, which influence the groundwater treatment time and cost, thus potentially affecting the final cleanup method selected. This article describes a constant-head test method and equipment used in the field to estimate relatively low hydraulic conductivities (K), an important hydrological property of the contaminated water-bearing zone used to estimate travel times.

APPROACH

A variety of methods are employed to measure K in the field. During a typical pumping test, groundwater is pumped from a well penetrating the desired zone at a constant rate, and the change in water levels is monitored in nearby wells. Alternatively, during a slug test, groundwater may be quickly added to or removed from a well, and the water level in the test well is monitored as it returns to its original level. Both techniques have their advantages and disadvantages. Pumping tests are difficult to perform in low K formations because the pumping rate may exceed the yield of the aquifer, causing the well to be pumped dry. The stress applied to the aquifer during a slug test typically penetrates only a short distance into the adjacent formation, suggesting the measured K may be influenced by conditions near the borehole (e.g., formation damage caused by drilling). The method presented here employs a specially designed Mariotte siphon system (Figure 1) to maintain a constant-hydraulic head on the test well during water injection. Observed changes in flow rate and water levels are used to estimate K.

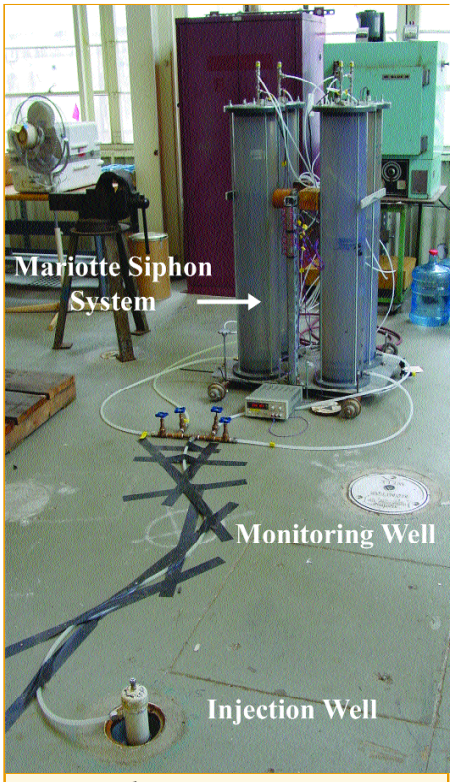


Figure 1. Photo of pressurized Mariotte siphon system and constant-head test configuration

ACCOMPLISHMENTS

Our equipment (Figure 1) differs from what is typically employed, which includes disc and Guelph permeameters, in that the test vessel is constructed to withstand higher working pressures and, therefore, can be operated at pressures exceeding one atmosphere (zero gauge pressure). This allows the test operator to deliver water to the well at a constant positive head up to 3 atmospheres (gauge) by connecting compressed air to the bubble tube instead of leaving it open to the atmosphere.

SIGNIFICANCE OF FINDINGS

The test equipment was successfully used to conduct a constant-head injection test lasting 60 days in duration. During this time period, water levels in adjacent observation wells, located up to 4.6 m from the injection point, increased by 0.3 to 1 m because of the 5.2 m injection head. Analysis of the test results produced estimates of K comparable to those produced from baseline slug tests conducted on the same wells. Constant-head tests have an advantage over pump tests in that they can be used to characterize low-yield porous materials. Compared to slug tests, this method stresses a much larger volume of the zone of interest, producing estimates of K that are less susceptible to error caused by wellbore damage and, therefore, more representative of the formation.

ACKNOWLEDGMENTS

This work is part of Berkeley Lab's Environmental Restoration Program, supported by the Assistant Secretary of the Office of Environmental Management, Office of Science and Technology, of the U.S. Department of Energy, under Contract No. DE-AC03-76-SF00098.

Studies Related to Deep Waste Injection

Chin-Fu Tsang and Dmitriy B. Silin
Contact: Chin-Fu Tsang, 510/486-5782, cftsang@lbl.gov

RESEARCH OBJECTIVES

The main purpose of the Underground Waste Injection project at Berkeley Lab is to develop new scientific approaches and methods related to underground injection of liquid wastes and to advise EPA on scientific aspects of injection regulation and permit process. In 2003, under the project an international symposium on Underground Injection Science and Technology will be organized, with attendees from 15 countries. One technical development in 2003 is the demonstration of a new pressure analysis method that allows the possibility of estimating the formation's hydraulic properties using regular operations data, to replace the currently-required annual shut-in tests. It is discussed below.

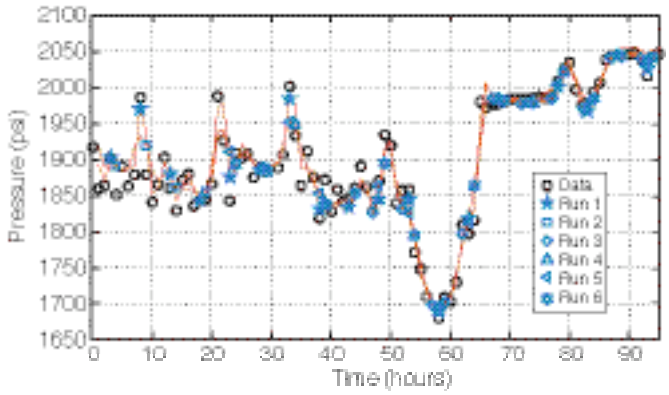


Figure 1. Hourly injection pressures from a deep injection well at an Ohio EPA site. Besides measured pressures (circles), the plot includes six matching curves obtained using ODA on different data intervals. All six curves practically collapse. Outside of the data matching intervals, the calculated curves provide accurate pressure predictions.

APPROACH

We have developed a new method, implemented in a code, ODA, to analyze the operations pumping rates and pumping pressure data (Silin and Tsang, 2002; 2003). To demonstrate its capability, first, the formation parameters are estimated from the regular injection operations data using the ODA code. Then, these results are compared with the results obtained independently from conventional analyses of fall-off tests.

RESULTS

The developed method has been applied to analyze several regular injection data sets obtained from four deep injection wells at an Ohio EPA site. The injection intervals are approximately 300 ft long and mostly consist of sandstone formations. The data fitting has been performed on various data intervals. The resulting estimates of the key hydraulic parameters are stable with respect to the selected data interval. Figure 1 shows the results of six different runs of the code on different matching intervals. In cases where the matching interval was significantly shorter than the whole data set, the extension of the calculated curve beyond this interval provides an accurate prediction of the actually measured pressures. In some cases, averaging of the data over a running time window helps to improve the quality of fitting. The smoothing of the data by such an averaging does not significantly affect the estimated values of the hydraulic parameters. Comparison of the results of analysis of conventional pressure fall-off tests obtained by our method with results obtained independently, using standard methods, shows that in most cases our estimates of the skin factor are significantly lower. We explain this by the fact that our approach rigorously accounts for the impact of pre-test pumping. Such an impact is neglected by the standard methods. The stability of our estimates makes them more credible than those of the standard methods, where the estimates strongly depend on the selection of the analyzed data interval.

SIGNIFICANCE OF FINDINGS

We have demonstrated that by applying the methods we have developed to regular operations data, we can obtain robust estimates of formation hydraulic properties. It implies that interruptions for conducting transient pressure well tests, which are required by regulations governing deep waste injection, can be significantly reduced or entirely replaced by regular data analysis. In addition to the consequent cost reduction, our method makes possible continuous monitoring of the formation properties, which means a significant safety enhancement with regard to timely detection of possible leakage or breakthrough of the liquid injectant.

RELATED PUBLICATIONS

Silin, D.B. and C.F. Tsang, Estimation of formation hydraulic properties accounting for pre-test injection or production operations. Journal of Hydrology, 265, 1–14, 2002.

Silin, D.B. and C.F. Tsang, A well-test analysis method accounting for pre-test operations. SPE Journal, 8(1), 22–30, 2003.

ACKNOWLEDGMENTS

This research has been supported by the U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water, Underground Injection Control Program, under an Interagency Agreement with the US Department of Energy under Contract No. DE-AC03-76SF00098.

Uranium Transformations in Contaminated Sediments

Jiamin Wan, Tetsu K. Tokunaga, Terry Hazen, Mary Firestone[1], Zuoping Zheng, Jasquelin Pena, Joern Larsen, and Eoin Brodie[1]
[1]University of California, Berkeley
Contact: Jiamin Wan, 510/486-6004, jmwan@lbl.gov

RESEARCH OBJECTIVES

Biogeochemical heterogeneity in the subsurface occurs because of transport limitations at many length scales. The question arises, when micro-environmental conditions vary significantly at the millimeter scale, where do specific biogeochemical processes occur, and how are they coupled? Within much of the subsurface, the spectrum of micro-environments is coupled through diffusive mass transfer. Thus, diffusion-limited domains are the simplest systems within which the full range of transformations can occur. Furthermore, such systems cannot be understood through characterization of bulk, volume-averaged properties because key gradients in chemical components and microbial communities are overlooked. In this research, we are investigating the biogeochemistry of uranium (U) and nitrate (NO_3^-) in diffusion-limited domains in order to understand the integrated effects of transport and biogeochemical reactions on transformations of these contaminants. Uranium and NO_3^- often occur as co-contaminants, and the reduction of soluble U(VI) to insoluble U(IV) in sediments is being considered as a strategy for *in situ* remediation. Pathways for U reoxidation need to be understood for us to critically evaluate reductive *in situ* remediation strategies. Our studies address three main segments of the subsurface U contamination cycle: (1) transport (sorption-release, diffusion, advection), (2) biogeochemistry of reduction (as influenced by NO_3^-), and (3) reoxidation.

APPROACH

Many studies are being conducted to evaluate both the individual aspects and integrated effects of the U cycle in contaminated sediments. Individual components under investigation include U(VI) sorption and release in batch systems, nitrate and U(VI) reduction in batch systems, and U(IV) reoxidation to U(VI). Column studies permit assessment of sorption-release and reduction-oxidation on overall U and NO_3^- transport. Experiments are also being done on historically contaminated and pristine soils from the NABIR Field Research Center at Oak Ridge, Tennessee.

ACCOMPLISHMENTS

The importance of calcite in suppressing U(VI) sorption into soils has been predicted and demonstrated (Zheng et al., 2003). Overall bacteria diversity in historically U-contaminated soils appeared to increase in response to lactate and NO_3^- additions, although the high diversity in *nir*S genes decreased. Lactate infusion into U-contaminated soils resulted in reduction to U(IV) within 30 days and was well reflected in redox potential measurements.

SIGNIFICANCE OF FINDINGS

The effect of calcite on suppressing U(VI) sorption was previously overlooked when standard experimental procedures were applied to slightly calcareous sediments. The sorption envelopes help explain the transient U(VI) diffusion measurements obtained in a related BES-supported study.

RELATED PUBLICATIONS

Tokunaga, T.K., J. Wan, T.C. Hazen, E. Schwartz, M.K. Firestone, S.R. Sutton, M. Newville, K.R. Olson, A. Lanzirotti, and W. Rao, Distribution of chromium contamination and microbial activity in soil aggregates. J. Environ. Qual., 32, 541–549, 2003.

Zheng, Z., T.K. Tokunaga, and J. Wan, Influence of calcium carbonate on sorption of U(VI) to soils, Environ. Sci. Technol., 2003 (submitted).

ACKNOWLEDGMENTS

This project is supported by the Director, Office of Science, Office of Biological and Environmental Research, Natural and Accelerated Bioremediation Research (NABIR) Program, of the U. S. Department of Energy under Contract No. DE-AC03-76-SF00098. Use of the Advanced Photon Source was supported by the DOE, Office of Science, Office of Basic Energy Sciences, under the same DOE contract number.

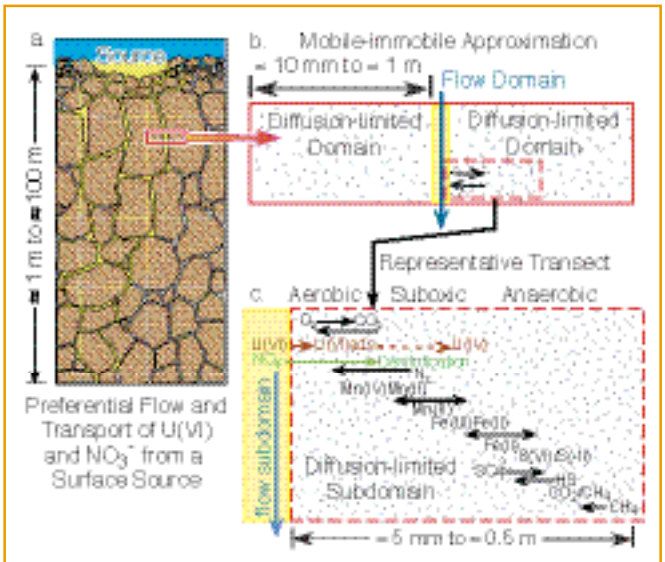


Figure 1. (a) Preferential flow and transport in the subsurface; (b) mobile-immobile approximation; (c) redox zonation within diffusion-limited domains

Geochemical Evolution of Highly Alkaline and Saline Tank Waste Plumes During Seepage Through Vadose Zone Sedments

Jiamin Wan, Tetsu K. Tokunaga, Joern T. Larsen, and Zuoping Zheng
Contact: Jiamin Wan, 510/486-6004, jmwan@lbl.gov

RESEARCH OBJECTIVES

Leakage of highly saline and alkaline radioactive waste solutions from storage tanks into underlying sediments is a serious problem at the Hanford Site in Washington State. Although it was found from field samples that pH values of the initially highly alkaline (pH 14) waste plumes dramatically decreased (to pH 10–7), understanding of the neutralization process was lacking. Since pH is a master geochemical variable, the behavior of waste plume contaminants, including their speciation, sorption, solubility, precipitation, and transport, can be reliably predicted only when the evolution of the pH profile is understood. This study focuses on the geochemical evolution of major geochemical parameters including pH, and addresses how pH evolved as the plumes propagated.

APPROACH

We designed a plume profiling method to obtain spatially and temporally direct measurements of plume geochemistry profiles. The influences of waste solution pH, ionic strength, and sediment type were also studied. To maximize the relevance of this laboratory study for understanding real field problems, most of the experiments involved infusion of synthetic waste solutions into sediment columns, thereby integrating the influences of reactions and transport.

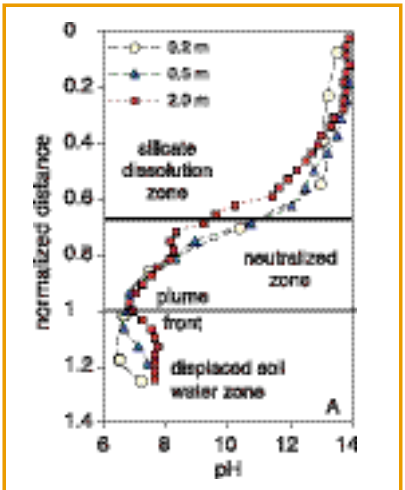


Figure 1. The pH profile along the 0.2, 0.5, and 2.0 m tall columns, with the distance axis normalized to the predicted plume front position

ACCOMPLISHMENTS

This study revealed that while the plume is connected to an actively leaking source, its profile spans the very broad range from pH 14 (influent waste pH) within the near-source region, down to pH 6.5 (lower than that of the initial soil solution) at the plume front (Figure 1). The plume can be divided into two zones: the Silicate Dissolution Zone (SDZ, pH 14–10), and Neutralized Zone (NZ, pH 10–7). After the plume source became inactive and the plume aged, pH values within the SDZ continued to decrease at a decreasing rate and eventually reached equilibrium at around pH 10—whereas the pH values in the original neutralized zone remained relatively unchanged. The major reactions responsible for the pH evolution of the waste plumes were identified, along with specific regions within the plumes where they occur.

SIGNIFICANCE OF FINDINGS

This laboratory study provides information on how pH evolved as tank waste plumes propagated. As a master geochemical variable, pH needs to be understood in order to predict the fate and transport of contaminants carried by waste plumes.

RELATED PUBLICATIONS

Wan, J., T.K. Tokunaga, J.T. Larsen, and R.J. Serne, Geochemical evolution of highly alkaline and saline tank waste plumes during seepage through vadose zone sediments. Geochim. Cosmochim. Acta, 2003 (in press).

Wan, J., J.T. Larsen, T.K. Tokunaga, and Z. Zheng, pH neutralization and zonation in alkaline-saline tank waste plumes. Environ. Sci. Technol., 2003 (submitted).

ACKNOWLEDGMENTS

This project is supported by the Assistant Secretary of the Office of Environmental Management, Office of Science and Technology, Environmental Management Science Program, of the U. S. Department of Energy under Contract No. DE-AC03-76-SF00098.

Modeling Geochemical Reactive Transport of Concentrated Aqueous Solutions in Variably Saturated Media

Guoxiang Zhang, Zuoping Zheng, and Jiamin Wan
Contact: Guoxiang Zhang, 510/486-4980, gxzhang@lbl.gov

RESEARCH OBJECTIVE

Concentrated aqueous solutions (CAS) occur in many natural and contaminated environments, such as in the leakage of highly concentrated $NaNO_3$ electrolytes stored at DOE's Hanford site. They are generally considered as solutions with ionic strength larger than 1 M and can be more than 10 M. The main objectives in this paper are (1) to develop a model that can simulate the coupled geochemical and transport processes of CAS by developing a Pitzer ion–interaction module and incorporating it into a previously developed computer code, BIO-CORE$^{2D©}$, (2) to verify the developed module and the implementation into BIO-CORE$^{2D©}$, and (3) to validate the developed model through simulating laboratory experiments.

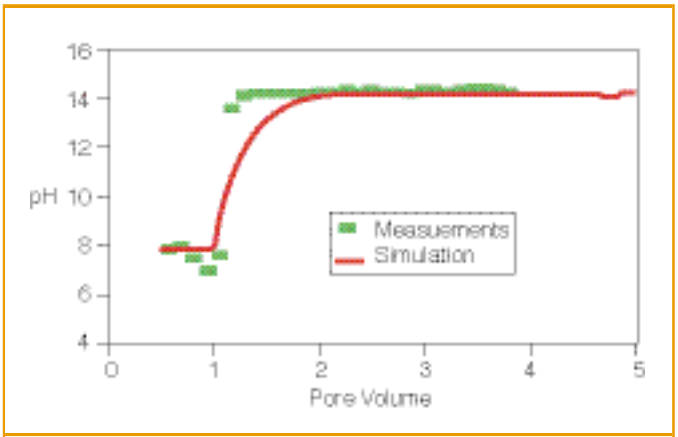


Figure.1. Simulated pH and measured pH of the effluent fluid during the injection of a highly alkaline-saline solution into a column filled with unsaturated sediments from the Hanford Site

APPROACH

The Pitzer ion-interaction model is considered the best representation of the ionic activity within CAS. In this study, a module of the Pitzer ion-interaction model is developed and implemented in a previously existing geochemical and microbiological reactive transport computer code, BIO-CORE$^{2D©}$ (Zhang, 2001). This code solves saturated-unsaturated flow, heat transfer, and solute transport coupled with chemical and microbial processes. A database storing Pitzer ion-interaction parameters was also developed. All parameters are temperature-dependent.

ACCOMPLISHMENTS

Several reported cases in the literature are used to verify the implementation of the Pitzer model. One of them calculates the activity coefficient of hydrochloric acid in a concentrated HCl-NaCl-KCl-H_2O system (298.15 K), at ionic strengths of 4, 5, 6, and 7 mol/kg, respectively, as a function of KCl concentration. We compared model results to the experimental data. Another case reports calculation of the activity coefficient of NaCl in a concentrated aqueous NaCl-Na_2SO_4-H_2O system—at ionic strengths of 2, 3, 4, and 6; and at 298.15 K and 318.15 K, respectively, as a function of Na_2SO_4 concentration. The results show that the activity coefficients calculated by BIO-CORE$^{2D©}$ are fairly close to the measurements. Wan et al. (2002) carried out a column experiment to understand the chemical interactions taking place in sediments from the Hanford Site during leakage of highly alkaline-saline solutions. In this experiment, highly alkaline-saline solution was injected into a column filled with unsaturated sediments from the Hanford Site. The experiment was modeled using BIO-CORE$^{2D©}$, and the results match the measured chemical composition of the effluent water. Figure 1 shows that the simulated pH matches the measured pH well. This result helps to improve our understanding of mineral precipitation and cation exchange processes during leakage of the tank waste solutions into sediments.

SIGNIFICANCE OF FINDING

The Pitzer phenomenological theory, as a basis for calculating ionic activities in concentrated aqueous solutions, is adequate for modeling high–ionic–strength problems. The Pitzer–type model generally reproduces the observed concentration trends for the Hanford case in which highly alkaline-saline solutions have leaked into sediments. Discrepancies could be attributed to uncertainties in cation exchange coefficients, surface areas, kinetics, and other thermodynamic data used in the model, as well as measurement errors.

RELATED PUBLICATIONS

Wan, J., T.K. Tokunaga, and J.T. Larsen, 2002, Evolution of REDOX tank waste plumes in Hanford vadose zone: A conceptual model developed through reactive transport studies, 2002 (submitted).

Zhang, G., 2001, Nonisothermal hydrobiogeochemical models in porous media. Ph.D. dissertation, University of La Coruña, Spain.

ACKNOWLEDGMENTS

This research is provided by the Assistant Secretary of the Office of Environmental Management, Office of Science and Technology, Environmental Management Science Program, of the U.S. Department of Energy under Contract No. DE-AC03-76SF-00098.

Berkeley Lab Site Modeling

Quanlin Zhou, Jens T. Birkholzer, Iraj Javandel, and Preston D. Jordan
Contact: Quanlin Zhou, 510/486-5344, qlzhou@lbl.gov

RESEARCH OBJECTIVES

In the late 1980s, groundwater contamination was detected at the original site of Berkeley Lab (Old Town Area). A detailed investigation was conducted to locate the source and extent of the contamination. Interim corrective measures were initiated where appropriate and required, typically directed towards removing the source of contamination and installing groundwater collection trenches downstream of the plumes, limiting further spreading of contaminants. To provide a basis for predicting the fate of contaminants, we developed a transient groundwater flow model for the complex hydrogeological situation in this area. The objective of this work is to improve our understanding of flow patterns and contaminant transport in the Old Town Area, to support the decision-making processes for remediation measures.

APPROACH

In addition to the complex hydrogeology—featuring several geologic units with strongly varying thicknesses, slopes, and properties—groundwater flow is strongly affected by seasonal patterns, by local recharge from leaking storm drains, and by significant water recharge from steep hills located in the upstream direction. A hydrogeologic model was developed from geologic information obtained from more than 100 boreholes and outcrop maps. Boundary conditions for this model were established from water levels collected from a large set of monitoring wells, subdrains, and deep trenches. Distribution of hydraulic conductivity was initially assigned based on the data compiled from single- and multiwell pumping tests. Recharge to groundwater was initially estimated from the type of land surface coverage (i.e., paved, under the building, or irrigated areas). Subsurface utility maps were also employed to locate and estimate potential leakage from corroded storm drains. Subsequently, some of the input data were adjusted, using calibration techniques enabling a very accurate hydrography of a large set of monitoring wells. Calibration was performed based on 1994–1996 water levels. The calibrated flow model was validated using a blind model prediction conducted for the period of July 1996–June 2000. A refined model was subsequently developed for the central area of the main contaminant plume. This refined model will be used as a tool to analyze and improve the current hydraulic measures conducted for contaminant remediation.

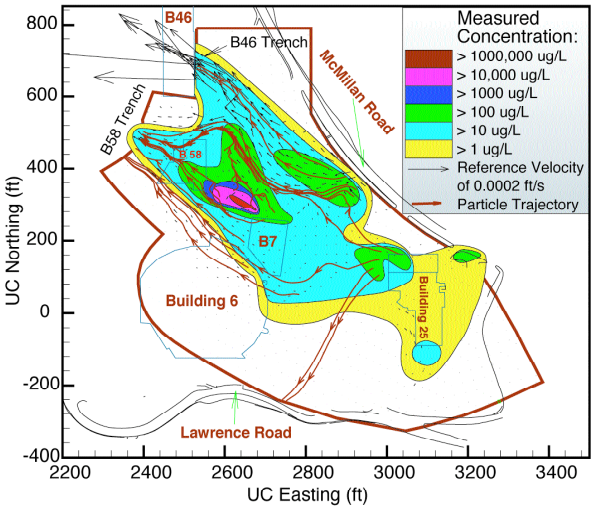


Figure 1. Simulated particle trajectories originating from contaminant plumes at steady-state flow rate (April 1998)

ACCOMPLISHMENTS

The calibrated hydrogeologic properties and recharge rates produced good agreement between the simulated and measured water table at about 40 observation wells and the flow rate at two water collection trenches. The calibrated "effective" porosity, which is much smaller than the actual physical porosity, represents the bulk effect of thin layers of relatively high hydraulic conductivity and large porosity, found in the mixed unit within bedrock of otherwise very low conductivity and porosity. This effective porosity thus leads to fast responses to water table changes with strong seasonal fluctuations. The validation results indicate that the developed model can accurately predict the complex groundwater flow at the Berkeley Lab site. Figure 1 shows the simulated velocity field and particle trajectories at July 1998, together with measured concentration contours. The simulated advective transport patterns and the measured extent of the plume are in good agreement.

SIGNIFICANCE OF FINDINGS

The developed model predicts groundwater flow in complex geological structures (ones with sharp changes in interfaces and water table gradients). It can improve our understanding of contaminant transport at the Berkeley Lab site and help us make better decisions about remediation measures for the Berkeley Lab Remediation Project.

RELATED PUBLICATIONS

Javandel, I., RCRA Facility Investigation Report, Module B, Lawrence Berkeley National Laboratory, Berkeley, California, 2000.

Zhou, Q., J. T. Birkholzer, I. Javandel, and P. D. Jordan, Simulation of Groundwater Flow at the LBNL site Using TOUGH2, LBNL-52512, Proceedings of TOUGH Symposium 2003, Berkeley, California, 2003.

ACKNOWLEDGMENTS

This work is part of Berkeley Lab's Environmental Restoration Program, supported by the Assistant Secretary of the Office of Environmental Management, Office of Science and Technology, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.